

# CHAPTER 18 ACID–BASE EQUILIBRIA

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- 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 ( $\text{H}_3\text{O}^+$ ) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion ( $\text{OH}^-$ ) in aqueous solution. Neutralization occurs when each  $\text{H}_3\text{O}^+$  molecule combines with an  $\text{OH}^-$  molecule to form 2 molecules of  $\text{H}_2\text{O}$ . Chemists found that the  $\Delta H_{\text{rxn}}$  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  $\text{NH}_3(g)$  and  $\text{HCl}(g)$  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.  $\text{NH}_3$  does not contain OH in its formula but produces  $\text{OH}^-$  ions in  $\text{H}_2\text{O}$ .
- 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,  $\text{H}_2\text{O}$ , is an **Arrhenius acid** because it produces  $\text{H}_3\text{O}^+$  ion in aqueous solution. Water is also an Arrhenius base because it produces the  $\text{OH}^-$  ion as well.  
b) Calcium hydroxide,  $\text{Ca}(\text{OH})_2$  is a base, not an acid.  
c) Phosphorous acid,  $\text{H}_3\text{PO}_3$ , is a weak **Arrhenius acid**. It is weak because the number of O atoms equals the number of ionizable H atoms.  
d) Hydroiodic acid, HI, is a strong **Arrhenius acid**.
- 18.6 **(b)**  $\text{H}_2\text{O}$  and **(d)**  $\text{H}_2\text{NNH}_2$  both are very weak Arrhenius bases.

- 18.7 a)  $\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NO}_2^-(aq)$

$$K_a = \frac{[\text{NO}_2^-][\text{H}_3\text{O}^+]}{[\text{HNO}_2]}$$

- b)  $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$

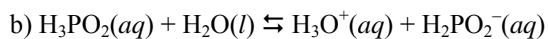
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$

- c)  $\text{HBrO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{BrO}_2^-(aq)$

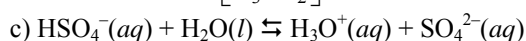
$$K_a = \frac{[\text{BrO}_2^-][\text{H}_3\text{O}^+]}{[\text{HBrO}_2]}$$

- 18.8 a)  $\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HPO}_4^{2-}(aq)$

$$K_a = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$$



$$K_a = \frac{[\text{H}_2\text{PO}_2^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_2]}$$



$$K_a = \frac{[\text{SO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{HSO}_4^-]}$$

18.9 Appendix C lists the  $K_a$  values. The larger the  $K_a$  value, the stronger the acid. Hydroiodic acid, HI, is not shown in Appendix C because  $K_a$  approaches infinity for strong acids and is not meaningful. Therefore, HI is the strongest acid and acetic acid,  $\text{CH}_3\text{COOH}$ , is the weakest:  **$\text{CH}_3\text{COOH} < \text{HF} < \text{HIO}_3 < \text{HI}$** .

18.10  **$\text{HCl} > \text{HNO}_2 > \text{HClO} > \text{HCN}$**

18.11 a) Arsenic acid,  $\text{H}_3\text{AsO}_4$ , is a **weak acid**. The number of O atoms is 4, which exceeds the number of ionizable H atoms, 3, by one. This identifies  $\text{H}_3\text{AsO}_4$  as a weak acid.

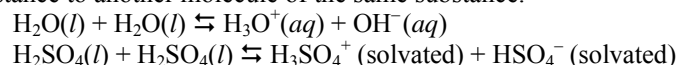
b) Strontium hydroxide,  $\text{Sr}(\text{OH})_2$ , is a **strong base**. Soluble compounds containing  $\text{OH}^-$  ions are strong bases.

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,  $\text{HClO}_4$ , is a **strong acid**.  $\text{HClO}_4$  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.

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

18.13 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.



18.14 a) pH increases by a value of 1  
b)  $[\text{H}_3\text{O}^+]$  increases by a factor of 1000

18.15 The lower the concentration of hydronium ( $\text{H}_3\text{O}^+$ ) 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  $K_a = 4 \times 10^{-5}$**  has a lower  $[\text{H}_3\text{O}^+]$  and higher pH.

b)  $\text{p}K_a$  is equal to  $-\log K_a$ . The smaller the  $K_a$ , the larger the  $\text{p}K_a$  is. So the **acid with the larger  $\text{p}K_a, 3.5$** , has a lower  $[\text{H}_3\text{O}^+]$  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  $[\text{H}_3\text{O}^+]$  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  $[\text{H}_3\text{O}^+]$  and higher pH.

e) Bases produce  $\text{OH}^-$  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)  $\text{pOH}$  equals  $-\log [\text{OH}^-]$ . At  $25^\circ\text{C}$ , the equilibrium constant for water ionization,  $K_w$ , equals  $1 \times 10^{-14}$  so  $14 = \text{pH} + \text{pOH}$ . As  $\text{pOH}$  decreases, pH increases. The solution of  **$\text{pOH} = 6.0$**  has the higher pH.

18.16 a) This problem can be approached two ways. Because NaOH is a strong base, the  $[\text{OH}^-]_{\text{eq}} = [\text{NaOH}]_{\text{init}}$ . One method involves calculating  $[\text{H}_3\text{O}^+]$  using from  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ , then calculating pH from the relationship  $\text{pH} = -\log [\text{H}_3\text{O}^+]$ . The other method involves calculating pOH and then using  $\text{pH} + \text{pOH} = 14.00$  to calculate pH.

First method:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0111} = 9.0090 \times 10^{-13} \text{ M (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.0090 \times 10^{-13}) = 12.04532 = \mathbf{12.05}$$

Second method:

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.0111) = 1.954677 \text{ (unrounded)}$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.954677 = 12.04532 = \mathbf{12.05}$$

With a  $\text{pH} > 7$ , 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:

$$[\text{H}_3\text{O}^+] = [\text{HCl}] = 1.35 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log (1.35 \times 10^{-3}) = 2.869666 \text{ (unrounded)}$$

$$\text{pOH} = 14.00 - 2.869666 = 11.130334 = \mathbf{11.13}$$

With a  $\text{pH} < 7$ , the solution is **acidic**.

18.17 a)  $\text{pH} = -\log (0.0333) = 1.47756 = \mathbf{1.478}$ ; **acidic**

b)  $\text{pOH} = -\log (0.0347) = 1.45967 = \mathbf{1.460}$ ; **basic**

18.18 a)  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.85} = 1.4125375 \times 10^{-10} = \mathbf{1.4 \times 10^{-10} \text{ M H}_3\text{O}^+}$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.85 = \mathbf{4.15}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.15} = 7.0794578 \times 10^{-5} = \mathbf{7.1 \times 10^{-5} \text{ M OH}^-}$$

b)  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.43 = \mathbf{4.57}$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.57} = 2.691535 \times 10^{-5} = \mathbf{2.7 \times 10^{-5} \text{ M H}_3\text{O}^+}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.43} = 3.7153523 \times 10^{-10} = \mathbf{3.7 \times 10^{-10} \text{ M OH}^-}$$

18.19 a)  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.77} = 1.69824 \times 10^{-5} = \mathbf{1.7 \times 10^{-5} \text{ M H}_3\text{O}^+}$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 4.77 = \mathbf{9.23}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.23} = 5.8884 \times 10^{-10} = \mathbf{5.9 \times 10^{-10} \text{ M OH}^-}$$

b)  $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.65 = \mathbf{8.35}$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.35} = 4.46684 \times 10^{-9} = \mathbf{4.5 \times 10^{-9} \text{ M H}_3\text{O}^+}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.65} = 2.23872 \times 10^{-6} = \mathbf{2.2 \times 10^{-6} \text{ M OH}^-}$$

18.20 The pH is increasing so the solution is becoming more basic. Therefore,  $\text{OH}^-$  ion is added to increase the pH. Since 1 mole of  $\text{H}_3\text{O}^+$  reacts with 1 mole of  $\text{OH}^-$ , the difference in  $[\text{H}_3\text{O}^+]$  would be equal to the  $[\text{OH}^-]$  added.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.52} = 3.01995 \times 10^{-5} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.25} = 5.623413 \times 10^{-6} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$3.01995 \times 10^{-5} \text{ M} - 5.623413 \times 10^{-6} \text{ M} = 2.4576 \times 10^{-5} \text{ M OH}^- \text{ must be added.}$$

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

18.21 The pH is decreasing so the solution is becoming more acidic. Therefore,  $\text{H}_3\text{O}^+$  ion is added to decrease the pH.

Since 1 mole of  $\text{H}_3\text{O}^+$  reacts with 1 mole of  $\text{OH}^-$ , the difference in  $[\text{OH}^-]$  would be equal to the  $[\text{H}_3\text{O}^+]$  added.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.92} = 1.20226 \times 10^{-9} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.33} = 4.67735 \times 10^{-7} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{Add } (4.67735 \times 10^{-7} \text{ M} - 1.20226 \times 10^{-9} \text{ M}) (87.5 \text{ mL}) (10^{-3} \text{ L} / 1 \text{ mL})$$

$$= 4.08216 \times 10^{-8} = \mathbf{4.1 \times 10^{-8} \text{ mol of H}_3\text{O}^+}$$

18.22 Scene A has a pH of 4.8.

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.8} = 1.58489 \times 10^{-5} \text{ M H}_3\text{O}^+$$

Scene B:

$$[\text{H}_3\text{O}^+] = (1.58489 \times 10^{-5} \text{ M H}_3\text{O}^+) \left( \frac{25 \text{ spheres}}{2 \text{ spheres}} \right) = 1.98 \times 10^{-4} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.98 \times 10^{-4}] = \mathbf{3.7}$$

- 18.23 Water in its pure form has only a very small conductance. Its electrical conductivity is due mostly to dissolved ions.
- 18.24 a) Heat is absorbed in an endothermic process:  $2 \text{H}_2\text{O}(l) + \text{heat} \rightarrow \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$ . 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  $[\text{H}^+]$  can be calculated. The problem specifies that the solution is neutral, meaning  $[\text{H}^+] = [\text{OH}^-]$ . A new  $K_w$  can then be calculated.  

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.80} = 1.58489 \times 10^{-7} \text{ M}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = 2.5 \times 10^{-14}$$
 For a neutral solution:  $\text{pH} = \text{pOH} = 6.80$
- 18.25 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,  $\text{NH}_3$ , and carbonate ion,  $\text{CO}_3^{2-}$ , 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.)
- 18.26 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.
- 18.27 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.
- 18.28  $\text{HB}(aq) + \text{A}^-(aq) \rightarrow \text{HA}(aq) + \text{B}^-(aq)$   
 The spontaneous direction of a Brønsted-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  $\text{B}^-$  in sample and less HB and  $\text{A}^-$ , **HB** must be the stronger acid and **A<sup>-</sup>** must be the stronger base.
- 18.29 An amphiprotic substance can act as either an acid or a base. In the presence of a strong base ( $\text{OH}^-$ ), the dihydrogen phosphate ion acts like an acid by donating hydrogen:  

$$\text{H}_2\text{PO}_4^-(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(aq) + \text{HPO}_4^{2-}(aq)$$
 In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:  

$$\text{H}_2\text{PO}_4^-(aq) + \text{HCl}(aq) \rightarrow \text{H}_3\text{PO}_4(aq) + \text{Cl}^-(aq)$$
- 18.30 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)  $\text{Cl}^-$    b)  $\text{HCO}_3^-$    c)  $\text{OH}^-$
- 18.31 a)  $\text{PO}_4^{3-}$    b)  $\text{NH}_3$    c)  $\text{S}^{2-}$
- 18.32 To derive the conjugate acid, add an H and increase the charge by 1.  
 a)  $\text{NH}_4^+$    b)  $\text{NH}_3$    c)  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+$
- 18.33 a)  $\text{OH}^-$    b)  $\text{HSO}_4^-$    c)  $\text{H}_3\text{O}^+$
- 18.34 The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid:  
 a) 
$$\text{NH}_3 + \text{H}_3\text{PO}_4 \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{PO}_4^-$$

$$\begin{array}{ccccccc} \text{base} & & \text{acid} & & \text{conjugate acid} & & \text{conjugate base} \end{array}$$
 Conjugate acid-base pairs:  $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$ ;  $\text{NH}_4^+/\text{NH}_3$

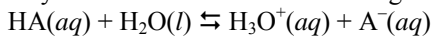
- b)  $\text{CH}_3\text{O}^- + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{OH} + \text{NH}_2^-$   
 base acid conjugate acid conjugate base  
 Conjugate acid-base pairs:  $\text{NH}_3/\text{NH}_2^-$ ;  $\text{CH}_3\text{OH}/\text{CH}_3\text{O}^-$
- c)  $\text{HPO}_4^{2-} + \text{HSO}_4^- \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{SO}_4^{2-}$   
 base acid conjugate acid conjugate base  
 Conjugate acid-base pairs:  $\text{HSO}_4^-/\text{SO}_4^{2-}$ ;  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$
- 18.35 a)  $\text{NH}_4^+ + \text{CN}^- \rightleftharpoons \text{NH}_3 + \text{HCN}$   
 acid base conjugate base conjugate acid  
 Conjugate acid-base pairs:  $\text{NH}_4^+/\text{NH}_3$ ;  $\text{HCN}/\text{CN}^-$
- b)  $\text{H}_2\text{O} + \text{HS}^- \rightleftharpoons \text{OH}^- + \text{H}_2\text{S}$   
 acid base conjugate base conjugate acid  
 Conjugate acid-base pairs:  $\text{H}_2\text{O}/\text{OH}^-$ ;  $\text{H}_2\text{S}/\text{HS}^-$
- c)  $\text{HSO}_3^- + \text{CH}_3\text{NH}_2 \rightleftharpoons \text{SO}_3^{2-} + \text{CH}_3\text{NH}_3^+$   
 acid base conjugate base conjugate acid  
 Conjugate acid-base pairs:  $\text{HSO}_3^-/\text{SO}_3^{2-}$ ;  $\text{CH}_3\text{NH}_3^+/\text{CH}_3\text{NH}_2$
- 18.36 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)  $\text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + 2\text{Na}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$   
 Net:  $\text{OH}^-(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{HPO}_4^{2-}(\text{aq})$   
 base acid conjugate acid conjugate base  
 Conjugate acid-base pairs:  $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$  and  $\text{H}_2\text{O}/\text{OH}^-$
- b)  $\text{K}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) + 2\text{K}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons 2\text{K}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{K}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$   
 Net:  $\text{HSO}_4^-(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{SO}_4^{2-}(\text{aq}) + \text{HCO}_3^-(\text{aq})$   
 acid base conjugate base conjugate acid  
 Conjugate acid-base pairs:  $\text{HSO}_4^-/\text{SO}_4^{2-}$  and  $\text{HCO}_3^-/\text{CO}_3^{2-}$
- 18.37 a)  $\text{H}_3\text{O}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 acid base conjugate acid conjugate base  
 Conjugate pairs:  $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ ;  $\text{HCO}_3^-/\text{CO}_3^{2-}$
- b)  $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 acid base conjugate base conjugate acid  
 Conjugate pairs:  $\text{NH}_4^+/\text{NH}_3$ ;  $\text{H}_2\text{O}/\text{OH}^-$
- 18.38 The conjugate pairs are  $\text{H}_2\text{S}$  (acid)/ $\text{HS}^-$  (base) and  $\text{HCl}$  (acid)/ $\text{Cl}^-$  (base). The reactions involve reacting one acid from one conjugate pair with the base from the other conjugate pair. Two reactions are possible:  
 (1)  $\text{HS}^- + \text{HCl} \rightleftharpoons \text{H}_2\text{S} + \text{Cl}^-$  and (2)  $\text{H}_2\text{S} + \text{Cl}^- \rightleftharpoons \text{HS}^- + \text{HCl}$   
 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.  $\text{HCl}$  is a strong acid and  $\text{H}_2\text{S}$  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  $K_c < 1$ .
- 18.39  $K_c > 1$ :  $\text{HNO}_3 + \text{F}^- \rightleftharpoons \text{NO}_3^- + \text{HF}$   
 $K_c < 1$ :  $\text{NO}_3^- + \text{HF} \rightleftharpoons \text{HNO}_3 + \text{F}^-$
- 18.40 a)  $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}^-$   
 strong acid stronger base weak acid weaker base  
 $\text{HCl}$  is ranked above  $\text{NH}_4^+$  in Figure 18.9 and is the stronger acid.  $\text{NH}_3$  is ranked above  $\text{Cl}^-$  and is the stronger base.  $\text{NH}_3$  is shown as a “stronger” base because it is stronger than  $\text{Cl}^-$ , 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  $K_c > 1$ . The stronger acid is more likely to donate a proton than the weaker acid.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]}$$

$$K_a = \frac{(1.51 \times 10^{-3})(1.51 \times 10^{-3})}{(0.14849)} = 1.53552 \times 10^{-5} = \mathbf{1.5 \times 10^{-5}}$$

18.46 Any weak acid dissociates according to the following equation:



$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.88} = 1.318 \times 10^{-5} \text{ M (unrounded)}$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = [\text{A}^-] = 1.318 \times 10^{-5} \text{ M, and } [\text{HA}] = (0.035 - 1.318 \times 10^{-5}) = 0.03499 \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

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

18.47 For a solution of a weak acid, the acid dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and  $\text{H}_3\text{O}^+$ . The acid dissociation reaction for  $\text{HNO}_2$  is:

Concentration	$\text{HNO}_2(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$	+	$\text{NO}_2^-(aq)$
Initial	0.60		—		0		0
Change	-x				+x		+x
Equilibrium	$0.60 - x$				x		x

(The  $\text{H}_3\text{O}^+$  contribution from water has been neglected.)

$$K_a = 7.1 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

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

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

$$x = 0.020639767 \text{ (unrounded)}$$

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

$$[\text{H}_3\text{O}^+] = [\text{NO}_2^-] = \mathbf{2.1 \times 10^{-2} \text{ M}}$$

The concentration of hydroxide ion is related to concentration of hydronium ion through the equilibrium for water:  $2 \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$  with  $K_w = 1.0 \times 10^{-14}$

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

18.48 For a solution of a weak acid, the acid dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and  $\text{H}_3\text{O}^+$ . The acid dissociation reaction for HF is:

Concentration	$\text{HF}(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$	+	$\text{F}^-(aq)$
Initial	0.75		—		0		0
Change	-x				+x		+x
Equilibrium	$0.75 - x$				x		x

(The  $\text{H}_3\text{O}^+$  contribution from water has been neglected.)

$$K_a = 6.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

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

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

$$x = 0.02258 \text{ (unrounded)}$$

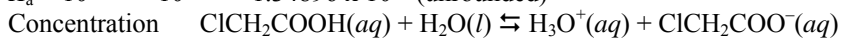
Check assumption:  $(0.02258/0.75) \times 100\% = 3\%$  error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = [\text{F}^-] = \mathbf{2.3 \times 10^{-2} \text{ M}}$$

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

- 18.49 Write a balanced chemical equation and equilibrium expression for the dissociation of chloroacetic acid and convert  $\text{p}K_a$  to  $K_a$ .

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



Initial	1.25	0	0
Change	-x	+x	+x
Equilibrium	$1.25 - x$	x	x

$$K_a = 1.34896 \times 10^{-3} = \frac{(\text{H}_3\text{O}^+)(\text{ClCH}_2\text{COO}^-)}{(\text{ClCH}_2\text{COOH})}$$

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

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

$$x = 0.04106336 \text{ (unrounded)}$$

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

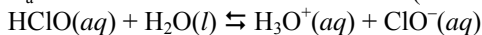
$$[\text{H}_3\text{O}^+] = [\text{ClCH}_2\text{COO}^-] = \mathbf{0.041 \text{ M}}$$

$$[\text{ClCH}_2\text{COOH}] = 1.25 - 0.04106336 = 1.20894 = \mathbf{1.21 \text{ M}}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.04106336) = 1.3865 = \mathbf{1.39}$$

- 18.50 Write a balanced chemical equation and equilibrium expression for the dissociation of hypochlorous acid and convert  $\text{p}K_a$  to  $K_a$ .

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



0.115 - x	x	x
-----------	---	---

$$K_a = 2.88403 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}$$

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

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

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

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

$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = \mathbf{5.8 \times 10^{-5} \text{ M}}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.75902 \times 10^{-5}) = 4.2396 = \mathbf{4.24}$$

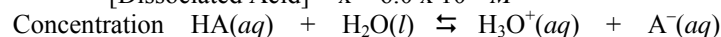


- 18.51 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.  
 a) The concentration of acid dissociated is equal to the equilibrium concentrations of  $A^-$  and  $H_3O^+$ . Then pH and  $[OH^-]$  are determined from  $[H_3O^+]$ .

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

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

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



$$\text{Initial: } \quad 0.20 \quad \quad \quad 0 \quad \quad 0$$

$$\text{Change: } \quad -x \quad \quad \quad +x \quad \quad +x$$

$$\text{Equilibrium: } \quad 0.20 - x \quad \quad \quad x \quad \quad x$$

$$[\text{Dissociated Acid}] = x = [H_3O^+] = 6.0 \times 10^{-3} M$$

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

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

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

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

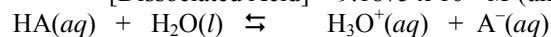
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(6.0 \times 10^{-3})(6.0 \times 10^{-3})}{(0.20 - 6.0 \times 10^{-3})} = 1.85567 \times 10^{-4} = 1.9 \times 10^{-4}$$

- 18.52 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  $[H_3O^+]$ .

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

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

$$[\text{Dissociated Acid}] = 9.1875 \times 10^{-2} M \text{ (unrounded)}$$



$$0.735 - x \quad \quad \quad x \quad \quad x$$

$$[\text{Dissociated Acid}] = x = [H_3O^+] = 9.19 \times 10^{-2} M$$

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

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

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

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

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

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

Concentration	HZ(aq)	+	H <sub>2</sub> O(l)	⇌	H <sub>3</sub> O <sup>+</sup> (aq)	+	Z <sup>-</sup> (aq)
Initial	0.075		—		0		0
Change	-x				+x		+x
Equilibrium	0.075 - x				x		x

(The H<sub>3</sub>O<sup>+</sup> contribution from water has been neglected.)

$$K_a = 2.55 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 4.3732 \times 10^{-3} \text{ (unrounded)}$$

Check assumption:  $(4.3732 \times 10^{-3}/0.075) \times 100\% = 6\%$  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.

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

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

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

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

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

$$x = 0.00425 \text{ or } -0.004503 \text{ (unrounded)}$$

(The -0.004503 value is not possible.)

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.00425) = 2.3716 = \mathbf{2.37}$$

b) Begin this part like part a.

Concentration	HZ(aq)	+	H <sub>2</sub> O(l)	⇌	H <sub>3</sub> O <sup>+</sup> (aq)	+	Z <sup>-</sup> (aq)
Initial	0.045		—		0		0
Change	-x				+x		+x
Equilibrium	0.045 - x				x		x

(The H<sub>3</sub>O<sup>+</sup> contribution from water has been neglected.)

$$K_a = 2.55 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 3.3875 \times 10^{-3} \text{ (unrounded)}$$

Check assumption:  $(3.3875 \times 10^{-3}/0.045) \times 100\% = 7.5\%$  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.

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

$$x^2 = (2.55 \times 10^{-4})(0.045 - x) = 1.1475 \times 10^{-5} - 2.55 \times 10^{-4}x$$

$$x^2 + 2.55 \times 10^{-4}x - 1.1475 \times 10^{-5} = 0$$

$$a = 1 \quad b = 2.55 \times 10^{-4} \quad c = -1.1475 \times 10^{-5}$$

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

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

$$x = 3.3899 \times 10^{-3} \text{ M H}_3\text{O}^+$$

$$[\text{OH}^-] = [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{3.3899 \times 10^{-3}} = 2.94994 \times 10^{-12} \text{ M}$$

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

18.54 Calculate  $K_a$  from  $\text{p}K_a$ .

$$K_a = 10^{-\text{p}K_a} = 10^{-4.89} = 1.2882 \times 10^{-5} \text{ (unrounded)}$$

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

Concentration	HQ(aq)	+	H <sub>2</sub> O(l)	⇌	H <sub>3</sub> O <sup>+</sup> (aq)	+	Q <sup>-</sup> (aq)
Initial	3.5 × 10 <sup>-2</sup>		—		0		0
Change	-x				+x		+x
Equilibrium	3.5 × 10 <sup>-2</sup> - x				x		x

(The H<sub>3</sub>O<sup>+</sup> contribution from water has been neglected.)

$$K_a = 1.2882 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Q}^-]}{[\text{HQ}]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 6.714685 \times 10^{-4} \text{ (unrounded)}$$

Check assumption:  $(6.714685 \times 10^{-4}/0.035) \times 100\% = 2\%$  error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = \mathbf{6.7 \times 10^{-4} \text{ M}}$$

b) Begin this problem like part a.

Concentration	HQ(aq)	+	H <sub>2</sub> O(l)	⇌	H <sub>3</sub> O <sup>+</sup> (aq)	+	Q <sup>-</sup> (aq)
Initial	0.65		—		0		0
Change	-x				+x		+x
Equilibrium	0.65 - x				x		x

(The H<sub>3</sub>O<sup>+</sup> contribution from water has been neglected.)

$$K_a = 1.2882 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Q}^-]}{[\text{HQ}]}$$

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

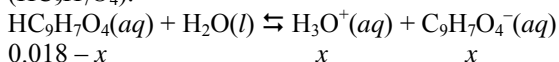
$$K_a = 1.2882 \times 10^{-5} = \frac{(x)(x)}{(0.65)}$$

$$[\text{H}_3\text{O}^+] = x = 2.893665 \times 10^{-3} \text{ (unrounded)}$$

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

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (2.893665 \times 10^{-3}) = 3.455825 \times 10^{-12} = \mathbf{3.5 \times 10^{-12} \text{ M}}$$

- 18.55 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of aspirin ( $\text{HC}_9\text{H}_7\text{O}_4$ ).



$$K_a = 3.6 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 2.54558 \times 10^{-3} \text{ (unrounded)}$$

Check assumption:  $(2.54558 \times 10^{-3}/0.018) \times 100\% = 14\%$  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.

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

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

$$a = 1 \quad b = 3.6 \times 10^{-4} \quad c = -6.48 \times 10^{-6}$$

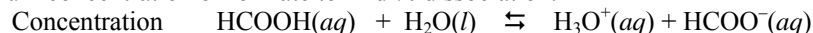
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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

$$x = 2.37194 \times 10^{-3} \text{ M } \text{H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.37194 \times 10^{-3}) = 2.624896 = \mathbf{2.62}$$

- 18.56 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.



$$\text{Initial} \quad \quad \quad 0.50 \quad \quad \quad 0 \quad \quad 0$$

$$\text{Change} \quad \quad \quad -x \quad \quad \quad +x \quad \quad +x$$

$$\text{Equilibrium} \quad \quad \quad 0.50 - x \quad \quad \quad x \quad \quad x$$

$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.50 - x)} \quad \text{Assume } x \text{ is small compared to } 0.50.$$

$$K_a = 1.8 \times 10^{-4} = \frac{(x)(x)}{(0.50)}$$

$$x = 9.4868 \times 10^{-3} \text{ (unrounded)}$$

Check assumption:  $(9.4868 \times 10^{-3}/0.50) \times 100\% = 2\%$  error, so the assumption is valid.

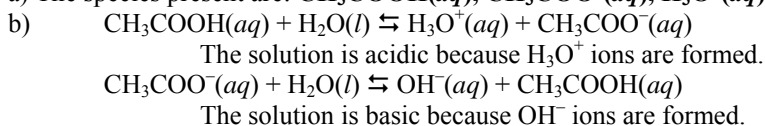
$$\text{Percent HCOOH Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \times 100\%$$

$$\text{Percent HCOOH Dissociated} = \frac{x}{0.50} \times 100\% = \frac{9.4868 \times 10^{-3}}{0.50} \times 100\% = 1.89736 = \mathbf{1.9\%}$$

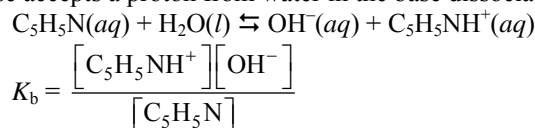
- 18.57 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an  $\text{H}^+$  and allows the base to act as a proton-acceptor.

18.58 The negative charge and lone pair of the anion in many cases is able to abstract a proton from water forming OH<sup>-</sup> ions. Non-basic anions are from strong acids and include Γ, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>.

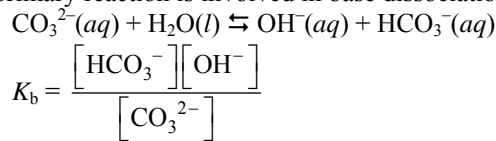
18.59 a) The species present are: **CH<sub>3</sub>COOH(aq), CH<sub>3</sub>COO<sup>-</sup>(aq), H<sub>3</sub>O<sup>+</sup>(aq), and OH<sup>-</sup>(aq).**



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

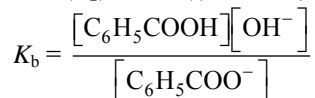


b) The primary reaction is involved in base dissociation of carbonate ion is:

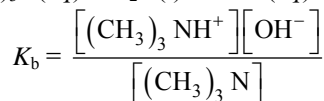


The bicarbonate can then also dissociate as a base, but this occurs to an insignificant amount in a solution of carbonate ions.

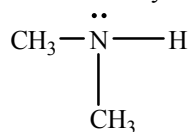
18.61 a)  $\text{C}_6\text{H}_5\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{C}_6\text{H}_5\text{COOH}(aq)$



b)  $(\text{CH}_3)_3\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + (\text{CH}_3)_3\text{NH}^+(aq)$



18.62 The formula of dimethylamine has two methyl (CH<sub>3</sub>-) groups attached to a nitrogen:

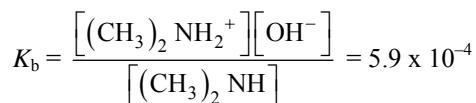


The nitrogen has a lone pair of electrons that will accept the proton from water in the base dissociation reaction:

The value for the dissociation constant is from Appendix C.

Concentration  $(\text{CH}_3)_2\text{NH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + (\text{CH}_3)_2\text{NH}_2^+(aq)$

Initial	0.070	0	0
Change	-x	+x	+x
Equilibrium	0.070 - x	x	x



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

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

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

Check assumption:  $(6.4265 \times 10^{-3}/0.070) \times 100\% = 9\%$  error, so the assumption is invalid.

The problem will need to be solved as a quadratic.

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

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

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

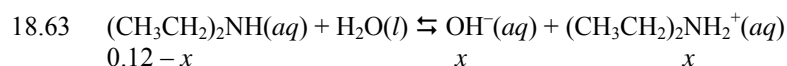
$$a = 1 \quad b = 5.9 \times 10^{-4} \quad c = -4.13 \times 10^{-5}$$

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

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.13827 \times 10^{-3}} = 1.629124 \times 10^{-12} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.629124 \times 10^{-12}) = 11.7880 = \mathbf{11.79}$$



$$K_b = \frac{[(\text{CH}_3\text{CH}_2)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3\text{CH}_2)_2\text{NH}]} = 8.6 \times 10^{-4}$$

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

The problem will need to be solved as a quadratic.

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

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

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

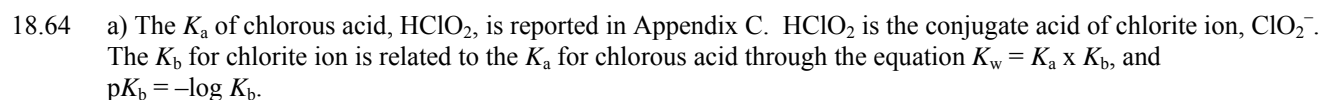
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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

$$x = 9.7378 \times 10^{-3} \text{ M OH}^- \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-] = (1.0 \times 10^{-14})/(9.7378 \times 10^{-3}) = 1.02692 \times 10^{-12} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.02692 \times 10^{-12}) = 11.98846 = \mathbf{11.99}$$



$$K_b \text{ of } \text{ClO}_2^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.1 \times 10^{-2}} = 9.0909 \times 10^{-13} \text{ (unrounded)}$$

$$\text{p}K_b = -\log (9.0909 \times 10^{-13}) = 12.04139 = \mathbf{12.04}$$

b) The  $K_b$  of dimethylamine,  $(\text{CH}_3)_2\text{NH}$ , is reported in Appendix C.  $(\text{CH}_3)_2\text{NH}$  is the conjugate base of  $(\text{CH}_3)_2\text{NH}_2^+$ . The  $K_a$  for  $(\text{CH}_3)_2\text{NH}_2^+$  is related to the  $K_b$  for  $(\text{CH}_3)_2\text{NH}$  through the equation  $K_w = K_a \times K_b$ , and  $\text{p}K_a = -\log K_a$ .

$$K_a \text{ of } (\text{CH}_3)_2\text{NH}_2^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.9 \times 10^{-4}} = 1.694915 \times 10^{-11} \text{ (unrounded)}$$

$$\text{p}K_a = -\log (1.694915 \times 10^{-11}) = 10.77085 = \mathbf{10.77}$$

- 18.65 a) The  $K_a$  of nitrous acid,  $\text{HNO}_2$ , is reported in Appendix C.  $\text{HNO}_2$  is the conjugate acid of nitrite ion,  $\text{NO}_2^-$ . The  $K_b$  for nitrite ion is related to the  $K_a$  for nitrous acid through the equation  $K_w = K_a \times K_b$ , and  $\text{p}K_b = -\log K_b$ .

$$K_b \text{ of } \text{NO}_2^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4084507 \times 10^{-11} \text{ (unrounded)}$$

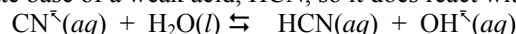
$$\text{p}K_b = -\log (1.4084507 \times 10^{-11}) = 10.851258 = \mathbf{10.85}$$

- b) The  $K_b$  of hydrazine,  $\text{H}_2\text{NNH}_2$ , is reported in the problem. Hydrazine is the conjugate base of  $\text{H}_2\text{N-NH}_3^+$ . The  $K_a$  for  $\text{H}_2\text{N-NH}_3^+$  is related to the  $K_b$  for  $\text{H}_2\text{NNH}_2$  through the equation  $K_w = K_a \times K_b$ , and  $\text{p}K_a = -\log K_a$ .

$$K_a \text{ of } \text{H}_2\text{N-NH}_3^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{8.5 \times 10^{-7}} = 1.17647 \times 10^{-8} \text{ (unrounded)}$$

$$\text{p}K_a = -\log (1.17647 \times 10^{-8}) = 7.9294 = \mathbf{7.93}$$

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



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

Concentration ( $M$ )       $\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$

Initial                    0.150                    —                    0                    0

Change                     $-x$                     —                     $+x$                      $+x$

Equilibrium               $0.150 - x$               —                     $x$                      $x$

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

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{\text{OH}^-} = \frac{1.0 \times 10^{-14}}{1.555 \times 10^{-3}} = 6.430868 \times 10^{-12} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.430868 \times 10^{-12}) = 11.19173 = \mathbf{11.19}$$

- b) The salt triethylammonium chloride in water dissociates into two ions:  $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$  and  $\text{Cl}^-$ . 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 ( $M$ )       $(\text{CH}_3\text{CH}_2)_3\text{NH}^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons (\text{CH}_3\text{CH}_2)_3\text{N}(aq) + \text{H}_3\text{O}^+(aq)$

Initial                    0.40                    —                    0                    0

Change                     $-x$                     —                     $+x$                      $+x$

Equilibrium               $0.40 - x$               —                     $x$                      $x$

$$K_a \text{ of } (\text{CH}_3\text{CH}_2)_3\text{NH}^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.2 \times 10^{-4}} = 1.9230769 \times 10^{-11} \text{ (unrounded)}$$

$$K_a = 1.9230769 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3\text{CH}_2)_3\text{N}]}{[(\text{CH}_3\text{CH}_2)_3\text{NH}^+]}$$

$$K_a = 1.9230769 \times 10^{-11} = \frac{(x)(x)}{(0.40 - x)} \quad \text{Assume } x \text{ is small compared to } 0.40: 0.40 - x = 0.40.$$

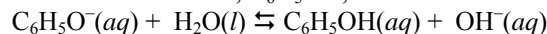
$$K_a = 1.9230769 \times 10^{-11} = \frac{(x)(x)}{(0.40)}$$

$$[\text{H}_3\text{O}^+] = x = 2.7735 \times 10^{-6} \text{ (unrounded)}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.7735 \times 10^{-6}) = 5.55697 = \mathbf{5.56}$$

- 18.67 a) Sodium phenolate, when placed in water, dissociates into sodium ions,  $\text{Na}^+$ , and phenolate ions,  $\text{C}_6\text{H}_5\text{O}^-$ . Sodium ion is the conjugate acid of a strong base,  $\text{NaOH}$ , so  $\text{Na}^+$  does not react with water. Phenolate ion is the conjugate base of a weak acid,  $\text{C}_6\text{H}_5\text{OH}$ , so it does react with the base dissociation reaction:



To find the pH first set up a reaction table and use  $K_b$  for  $\text{C}_6\text{H}_5\text{O}^-$  to calculate  $[\text{OH}^-]$ .

Concentration (M)	$\text{C}_6\text{H}_5\text{O}^-(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{C}_6\text{H}_5\text{OH}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.100		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.100 - x$		—		x		x

$$K_b \text{ of } \text{C}_6\text{H}_5\text{O}^- = K_w / K_a = (1.0 \times 10^{-14}) / (1.0 \times 10^{-10}) = 1.0 \times 10^{-4}$$

$$K_b = \frac{[\text{C}_6\text{H}_5\text{OH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{O}^-]} = 1.0 \times 10^{-4}$$

$$K_b = \frac{[x][x]}{[0.100 - x]} = 1.0 \times 10^{-4} \text{ Assume } x \text{ is small compared to } 0.100.$$

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

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

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

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (3.16227766 \times 10^{-3}) = 3.16227766 \times 10^{-12} \text{ M } \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.16227766 \times 10^{-12}) = \mathbf{11.50}$$

- b) The salt methylammonium bromide in water dissociates into two ions:  $\text{CH}_3\text{NH}_3^+$  and  $\text{Br}^-$ . 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)	$\text{CH}_3\text{NH}_3^+(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{CH}_3\text{NH}_2(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.15		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.15 - x$		—		x		x

$$K_a \text{ of } \text{CH}_3\text{NH}_3^+ = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.272727 \times 10^{-11} \text{ (unrounded)}$$

$$K_a = 2.272727 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{NH}_2]}{[\text{CH}_3\text{NH}_3^+]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 1.84637 \times 10^{-6} \text{ (unrounded)}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.84637 \times 10^{-6}) = 5.73368 = \mathbf{5.73}$$



18.68 First, calculate the initial molarity of  $\text{ClO}^-$ . Then, set up reaction table with base dissociation of  $\text{OCl}^-$ :

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

$$= 0.873186 \text{ M OCl}^- \text{ (unrounded)}$$

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

Concentration (M)	$\text{OCl}^-(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{HOCl}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.873186		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.873186 - x$		—		x		x

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

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

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

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

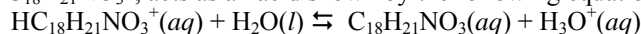
$$x = 5.4872 \times 10^{-4} = \mathbf{5.5 \times 10^{-4} \text{ M OH}^-}$$

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.4872 \times 10^{-4}} = 1.82242 \times 10^{-11} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.82242 \times 10^{-11}) = 10.73935 = \mathbf{10.74}$$

18.69 The cation ion,  $\text{HC}_{18}\text{H}_{21}\text{NO}_3^+$ , acts as an acid shown by the following equation:



Because  $\text{HC}_{18}\text{H}_{21}\text{NO}_3\text{Cl}$  is a soluble salt,  $[\text{HC}_{18}\text{H}_{21}\text{NO}_3^+] = [\text{HC}_{18}\text{H}_{21}\text{NO}_3\text{Cl}]$ . The chloride ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$\text{HC}_{18}\text{H}_{21}\text{NO}_3^+(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{C}_{18}\text{H}_{21}\text{NO}_3(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.050		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.050 - x$		—		x		x

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

$$K_a \text{ of HC}_{18}\text{H}_{21}\text{NO}_3^+ = K_w/K_b = (1.0 \times 10^{-14})/(1.58489 \times 10^{-6}) = 6.309586 \times 10^{-9} \text{ (unrounded)}$$

$$K_a = 6.309586 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{18}\text{H}_{21}\text{NO}_3]}{[\text{HC}_{18}\text{H}_{21}\text{NO}_3^+]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 1.7761737 \times 10^{-5} \text{ (unrounded)}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.7761737 \times 10^{-5}) = 4.75051 = \mathbf{4.75}$$

18.70 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  $\text{H}^+$  and making the  $\text{H}^+$  more easily transferred to a surrounding water molecule to make  $\text{H}_3\text{O}^+$ .

- 18.71 As the nonmetal increases in size, its bond to hydrogen becomes longer and weaker, so that  $\text{H}^+$  is more easily lost, and a stronger acid results.
- 18.72 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.
- 18.73 The two factors that explain the greater acid strength of  $\text{HClO}_4$  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  $\text{HClO}_4$  less tightly held by the oxygen than the H in  $\text{HIO}$ .  
 2) Perchloric acid has more oxygen atoms than  $\text{HIO}$ , which leads to a greater shift in electron density from the hydrogen atom to the oxygens making the H in  $\text{HClO}_4$  more susceptible to transfer to a base.
- 18.74 a)  $\text{H}_2\text{Se}$ , hydrogen selenide, is a stronger acid than  $\text{H}_3\text{As}$ , arsenic hydride, because Se is more electronegative than As.  
 b)  $\text{B}(\text{OH})_3$ , boric acid also written as  $\text{H}_3\text{BO}_3$ , is a stronger acid than  $\text{Al}(\text{OH})_3$ , aluminum hydroxide, because boron is more electronegative than aluminum.  
 c)  $\text{HBrO}_2$ , bromous acid, is a stronger acid than  $\text{HBrO}$ , hypobromous acid, because there are more oxygen atoms in  $\text{HBrO}_2$  than in  $\text{HBrO}$ .
- 18.75 a)  $\text{HBr}$                       b)  $\text{H}_3\text{AsO}_4$                       c)  $\text{HNO}_2$
- 18.76 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,  $\text{CuSO}_4$ , contains  $\text{Cu}^{2+}$  ion with  $K_a = 3 \times 10^{-8}$ . Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3$ , contains  $\text{Al}^{3+}$  ion with  $K_a = 1 \times 10^{-5}$ . The concentrations of  $\text{Cu}^{2+}$  and  $\text{Al}^{3+}$  are equal, but the  $K_a$  of  $\text{Al}_2(\text{SO}_4)_3$  is almost three orders of magnitude greater. Therefore, **0.25 M  $\text{Al}_2(\text{SO}_4)_3$**  is the stronger acid and would have the lower pH.  
 b) Zinc chloride,  $\text{ZnCl}_2$ , contains the  $\text{Zn}^{2+}$  ion with  $K_a = 1 \times 10^{-9}$ . Lead chloride,  $\text{PbCl}_2$ , contains the  $\text{Pb}^{2+}$  ion with  $K_a = 3 \times 10^{-8}$ . Since both solutions have the same concentration, and  $K_a(\text{Pb}^{2+}) > K_a(\text{Zn}^{2+})$ , **0.3 M  $\text{PbCl}_2$**  is the stronger acid and would have the lower pH.
- 18.77 a)  $\text{NaCl}$                       b)  $\text{Co}(\text{NO}_3)_2$
- 18.78 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.  
Basic salt:  $\text{KCN}$  ( $\text{K}^+$  is the cation from the strong base  $\text{KOH}$ ;  $\text{CN}^-$  is the anion from the weak acid,  $\text{HCN}$ .)  
Acid salt:  $\text{FeCl}_3$  or  $\text{NH}_4\text{NO}_3$  ( $\text{Fe}^{3+}$  is a small, highly charged metal cation and  $\text{Cl}^-$  is the anion of the strong acid  $\text{HCl}$ ;  $\text{NH}_4^+$  is the cation of the weak base  $\text{NH}_3$  while  $\text{NO}_3^-$  is the anion of the strong acid  $\text{HNO}_3$ .)  
Neutral salt:  $\text{KNO}_3$  ( $\text{K}^+$  is the cation of the strong base  $\text{KOH}$  while  $\text{NO}_3^-$  is the anion of the strong acid  $\text{HNO}_3$ .)
- 18.79 Sodium fluoride,  $\text{NaF}$ , contains the cation of a strong base,  $\text{NaOH}$ , and anion of a weak acid,  $\text{HF}$ . This combination yields a salt that is basic in aqueous solution as the  $\text{F}^-$  ion acts as a base:  

$$\text{F}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$$
 Sodium chloride,  $\text{NaCl}$ , is the salt of a strong base,  $\text{NaOH}$ , and strong acid,  $\text{HCl}$ . This combination yields a salt that is neutral in aqueous solution as neither  $\text{Na}^+$  or  $\text{Cl}^-$  react in water to change the  $[\text{H}^+]$ .
- 18.80 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 ( $\text{CH}_3\text{COOH}$ ) is  $1.8 \times 10^{-5}$ , and the  $K_b$  for the conjugate base ( $\text{NH}_3$ ) is  $1.76 \times 10^{-5}$ .

- 18.81 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)  $\text{KBr}(s) + \text{H}_2\text{O}(l) \rightarrow \text{K}^+(aq) + \text{Br}^-(aq)$   
 $\text{K}^+$  is the conjugate acid of a strong base, so it does not influence pH.  
 $\text{Br}^-$  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 pH of pure water with a **neutral** pH.
- b)  $\text{NH}_4\text{I}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NH}_4^+(aq) + \text{I}^-(aq)$   
 $\text{NH}_4^+$  is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce  $\text{H}_3\text{O}^+$  as represented by the acid dissociation reaction:  

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$$
 $\text{I}^-$  is the conjugate base of a strong acid, so it will not influence the pH.  
 The production of  $\text{H}_3\text{O}^+$  from the ammonium ion makes the solution of  $\text{NH}_4\text{I}$  **acidic**.
- c)  $\text{KCN}(s) + \text{H}_2\text{O}(l) \rightarrow \text{K}^+(aq) + \text{CN}^-(aq)$   
 $\text{K}^+$  is the conjugate acid of a strong base, so it does not influence pH.  
 $\text{CN}^-$  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:  

$$\text{CN}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(aq) + \text{OH}^-(aq)$$
 Hydroxide ions are produced in this equilibrium so solution will be **basic**.
- 18.82 a)  $\text{Cr}(\text{NO}_3)_3(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + 3\text{NO}_3^-(aq)$   

$$\text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cr}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}(aq) + \text{H}_3\text{O}^+(aq) \quad \text{acidic}$$
- b)  $\text{NaHS}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Na}^+(aq) + \text{HS}^-(aq)$   

$$\text{HS}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{S}(aq) \quad \text{basic}$$
- c)  $\text{Zn}(\text{CH}_3\text{COO})_2(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Zn}(\text{H}_2\text{O})_n^{2+}(aq) + 2\text{CH}_3\text{COO}^-(aq)$   

$$\text{Zn}(\text{H}_2\text{O})_n^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Zn}(\text{H}_2\text{O})_{n-1}\text{OH}^+(aq) + \text{H}_3\text{O}^+(aq)$$

$$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{CH}_3\text{COOH}(aq)$$

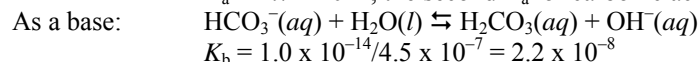
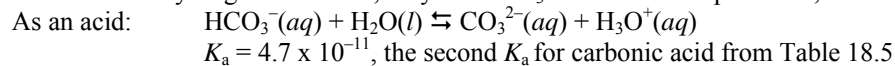
$$K_a(\text{Zn}(\text{H}_2\text{O})_n^{2+}) = 1 \times 10^{-9}$$

$$K_b(\text{CH}_3\text{COO}^-) = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.5556 \times 10^{-10} \quad (\text{unrounded})$$
 The two  $K$  values are similar, so the solution is close to **neutral**.
- 18.83 a) Order of increasing pH:  **$\text{KNO}_3 < \text{K}_2\text{SO}_3 < \text{K}_2\text{S}$**  (assuming concentrations equivalent)  
 Potassium nitrate,  $\text{KNO}_3$ , 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,  $\text{K}_2\text{SO}_3$ , and potassium sulfide,  $\text{K}_2\text{S}$ , 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  $\text{HSO}_3^-$  is  $6.5 \times 10^{-8}$  from Table 18.5, so  $K_b$  for  $\text{SO}_3^{2-}$  is  $1.5 \times 10^{-7}$ , which indicates that sulfite ion is a weak base.  $K_a$  for  $\text{HS}^-$  is  $1 \times 10^{-17}$  from Table 18.5, so sulfide ion has a  $K_b$  equal to  $1 \times 10^3$ . 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:  **$\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$**   
 In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:  

$$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)$$
 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  $\text{HSO}_4^-$  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,  $\text{HSO}_4^-$  is the conjugate base of a strong acid, so it will not influence pH. As an acid,  $\text{HSO}_4^-$  is the conjugate acid of a weak base, so the acid dissociation applies.  

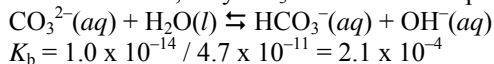
$$\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{SO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = 1.2 \times 10^{-2}$$

In solutions of sodium hydrogen carbonate, only the  $\text{HCO}_3^-$  will influence pH and it, like  $\text{HSO}_4^-$ , is amphoteric:



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

In a solution of sodium carbonate, only  $\text{CO}_3^{2-}$  will influence pH by acting as a weak base:



Therefore, the solution of sodium carbonate is basic.

Two of the solutions are acidic. Since the  $K_a$  of  $\text{HSO}_4^-$  is greater than that of  $\text{NH}_4^+$ , the solution of sodium hydrogen sulfate has a lower pH than the solution of ammonium nitrate, assuming the concentrations are relatively close.

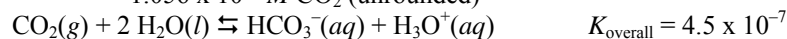
Two of the solutions are basic. Since the  $K_b$  of  $\text{CO}_3^{2-}$  is greater than that of  $\text{HCO}_3^-$ , the solution of sodium carbonate has a higher pH than the solution of sodium hydrogen carbonate, assuming concentrations are not extremely different.

- 18.84 a)  $\text{KClO}_2 > \text{MgCl}_2 > \text{NH}_4\text{Cl}$   
b)  $\text{NaBrO}_2 > \text{NaClO}_2 > \text{NaBr} > \text{NH}_4\text{Br}$
- 18.85 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.
- 18.86 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 except that for a Brønsted-Lowry base the acceptor is a proton.
- 18.87 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, water molecules solvate metal ions very well:  
$$\text{Zn}^{2+}(aq) + 4 \text{H}_2\text{O}(l) \rightleftharpoons \text{Zn}(\text{H}_2\text{O})_6^{2+}(aq)$$
  
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  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  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  $\text{Cu}(\text{CN})_4^{2-}$  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**.
- 18.88 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.
- 18.89 a)  $\text{NH}_3$  can only act as a Brønsted-Lowry or Lewis base.  
b)  $\text{AlCl}_3$  can only act as a Lewis acid.
- 18.90 a)  $\text{Cu}^{2+}$  is a **Lewis acid** because it accepts electron pairs from molecules such as water.  
b)  $\text{Cl}^-$  is a **Lewis base** because it has lone pairs of electrons it can donate to a Lewis acid.  
c) Tin(II) chloride,  $\text{SnCl}_2$ , 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,  $\text{OF}_2$ , 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.
- 18.91 a) **Lewis acid**    b) **Lewis base**    c) **Lewis base**    d) **Lewis acid**



- 18.97 a) step (1):  $\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)$  **Lewis**  
 step (2):  $\text{H}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{H}_3\text{O}^+(aq)$  **Brønsted-Lowry and Lewis**

b) Molarity  $\text{CO}_2 = k_{\text{Henry}} P_{\text{carbon dioxide}} = (0.033 \text{ mol/L}\cdot\text{atm}) (3.2 \times 10^{-4} \text{ atm})$   
 $= 1.056 \times 10^{-5} \text{ M CO}_2$  (unrounded)



$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{[1.056 \times 10^{-5} - x]}$$

The problem will need to be solved as a quadratic.

$$x^2 = (4.5 \times 10^{-7})(1.056 \times 10^{-5} - x) = 4.752 \times 10^{-12} - 4.5 \times 10^{-7} x$$

$$x^2 + 4.5 \times 10^{-7} x - 4.752 \times 10^{-12} = 0$$

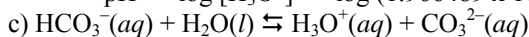
$$a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -4.752 \times 10^{-12}$$

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

$$x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-4.752 \times 10^{-12})}}{2(1)}$$

$$x = 1.966489 \times 10^{-6} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.966489 \times 10^{-6}) = 5.7063 = \mathbf{5.71}$$



$$K_a = 4.7 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

Use the unrounded  $x$  from part b.

$$K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{[1.966489 \times 10^{-6} + x][x]}{[1.966489 \times 10^{-6} - x]} \quad \text{Assume } x \text{ is small compared to } 2 \times 10^{-6}$$

$$K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{[1.966489 \times 10^{-6}][x]}{[1.966489 \times 10^{-6}]}$$

$$[\text{CO}_3^{2-}] = \mathbf{4.5 \times 10^{-11} \text{ M CO}_3^{2-}}$$

d) New molarity  $\text{CO}_2 = 2 k_{\text{Henry}} P_{\text{carbon dioxide}} = 2 (0.033 \text{ mol/L}\cdot\text{atm}) (3.2 \times 10^{-4} \text{ atm})$   
 $= 2.112 \times 10^{-5} \text{ M CO}_2$  (unrounded)

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{[2.112 \times 10^{-5} - x]}$$

The problem will need to be solved as a quadratic.

$$x^2 = (4.5 \times 10^{-7})(2.112 \times 10^{-5} - x) = 9.504 \times 10^{-12} - 4.5 \times 10^{-7} x$$

$$x^2 + 4.5 \times 10^{-7} x - 9.504 \times 10^{-12} = 0$$

$$a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -9.504 \times 10^{-12}$$

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

$$x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-9.504 \times 10^{-12})}}{2(1)}$$

$$x = 2.866 \times 10^{-6} \text{ M } \text{H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.866 \times 10^{-6}) = 5.5427 = \mathbf{5.54}$$

18.98 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ).

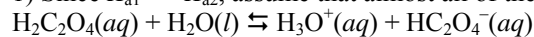


$$K_{a1} = 5.6 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

$$K_{a2} = 5.4 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]}$$

Assumption:

1) Since  $K_{a1} \gg K_{a2}$ , assume that almost all of the  $\text{H}_3\text{O}^+$  comes from the first dissociation.



$$0.200 - x \qquad \qquad \qquad x \qquad \qquad \qquad x$$

$$K_{a1} = 5.6 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]}$$

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

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

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

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = [\text{HC}_2\text{O}_4^-] = x = \mathbf{8.1 \times 10^{-2} \text{ M}}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.1471 \times 10^{-2}) = 1.08899 = \mathbf{1.09}$$

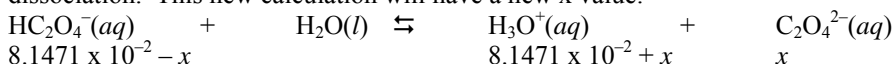
$$[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(8.1471 \times 10^{-2}) = 1.22743 \times 10^{-13} = \mathbf{1.2 \times 10^{-13} \text{ M}}$$

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

$$[\text{H}_2\text{C}_2\text{O}_4] = (0.200 - 8.1471 \times 10^{-2}) \text{ M} = 0.118529 = \mathbf{0.12 \text{ M}}$$

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.



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

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

$$K_{a2} = 5.4 \times 10^{-5} = \frac{(8.1471 \times 10^{-2})(x)}{(8.1471 \times 10^{-2})} \quad \text{Assume } x \text{ is small compared to } 8.1471 \times 10^{-2}.$$

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

- 18.99 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  $5s$  and  $5p$  orbitals. The  $5d$  orbitals are empty and available for the bond with trimethylamine.

- 18.100 Hydrochloric acid is a strong acid that almost 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:

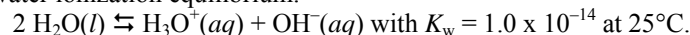
$$pH = -\log(1.0 \times 10^{-5}) = \mathbf{5.00 = pH}$$

A 1:10 dilution means that the chemist takes 1 mL of the  $1.0 \times 10^{-5} M$  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:  $M_1V_1 = M_2V_2$   
 $(1.0 \times 10^{-5} M)(1.0 \text{ mL}) = (x)(10. \text{ mL})$   
 $[H_3O^+]_{HCl} = 1.0 \times 10^{-6} M H_3O^+$   
 $pH = -\log(1.0 \times 10^{-6}) = \mathbf{6.00}$

Dilution 2:  
 $(1.0 \times 10^{-6} M)(1.0 \text{ mL}) = (x)(10. \text{ mL})$   
 $[H_3O^+]_{HCl} = 1.0 \times 10^{-7} M H_3O^+$

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:



The dilution gives an initial  $[H_3O^+]$  of  $1.0 \times 10^{-7} M$ . Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$OH^-(aq)$
Initial	—		$1 \times 10^{-7}$		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:  $x^2 + 1.0 \times 10^{-7}x - 1.0 \times 10^{-14} = 0$

$$a = 1 \quad b = 1.0 \times 10^{-7} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{(1.0 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 6.1803 \times 10^{-8} \text{ (unrounded)}$$

$$[H_3O^+] = (1.0 \times 10^{-7} + x) M = (1.0 \times 10^{-7} + 6.1803 \times 10^{-8}) M = 1.61803 \times 10^{-7} M H_3O^+ \text{ (unrounded)}$$

$$pH = -\log [H_3O^+] = -\log (1.61803 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$$



Dilution 3:

$$(1.0 \times 10^{-7} M)(1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-8} M \text{ H}_3\text{O}^+$$

The dilution gives an initial  $[\text{H}_3\text{O}^+]$  of  $1.0 \times 10^{-8} M$ . Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 \text{ H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		$1 \times 10^{-8}$		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-8} + x$		x

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-8} + x)(x) = 1.0 \times 10^{-14}$$

$$\text{Set up as a quadratic equation: } x^2 + 1.0 \times 10^{-8}x - 1.0 \times 10^{-14} = 0$$

$$a = 1 \quad b = 1.0 \times 10^{-8} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.51249 \times 10^{-8} \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-8} + x) M = (1.0 \times 10^{-8} + 9.51249 \times 10^{-8}) M = 1.051249 \times 10^{-7} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.051249 \times 10^{-7}) = 6.97829 = \mathbf{6.98}$$

Dilution 4:

$$(1.0 \times 10^{-8} M)(1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-9} M \text{ H}_3\text{O}^+$$

The dilution gives an initial  $[\text{H}_3\text{O}^+]$  of  $1.0 \times 10^{-9} M$ . Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2 \text{ H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		$1 \times 10^{-9}$		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-9} + x$		x

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-9} + x)(x) = 1.0 \times 10^{-14}$$

$$\text{Set up as a quadratic equation: } x^2 + 1.0 \times 10^{-9}x - 1.0 \times 10^{-14} = 0$$

$$a = 1 \quad b = 1.0 \times 10^{-9} \quad c = -1.0 \times 10^{-14}$$

$$x = \frac{-1.0 \times 10^{-9} \pm \sqrt{(1.0 \times 10^{-9})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$x = 9.95012 \times 10^{-8} \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) M = 1.00512 \times 10^{-7} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.00512 \times 10^{-7}) = 6.99778 = \mathbf{7.00}$$

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.

- 18.101 Compare the contribution of each acid by calculating the concentration of  $\text{H}_3\text{O}^+$  produced by each. For 3% hydrogen peroxide, first find initial molarity of  $\text{H}_2\text{O}_2$ , assuming the density is 1.00 g/mL (the density of water).

$$M \text{ H}_2\text{O}_2 = \left( \frac{1.00 \text{ g}}{\text{mL}} \right) \left( \frac{3\% \text{ H}_2\text{O}_2}{100\%} \right) \left( \frac{1 \text{ mol H}_2\text{O}_2}{34.02 \text{ g H}_2\text{O}_2} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.881834 M \text{ H}_2\text{O}_2 \text{ (unrounded)}$$

$$\text{Find } K_a \text{ from } \text{p}K_a: K_a = 10^{-\text{p}K_a} = 10^{-11.75} = 1.778279 \times 10^{-12} \text{ (unrounded)}$$

	$\text{H}_2\text{O}_2$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_2\text{O}^+$	+	$\text{HO}_2^-$
Initial	0.881834		—		0		0
Change	-x		—		+x		+x
Equilibrium	$0.881834 - x$		—		x		x

$$K_a = 1.778279 \times 10^{-12} = \frac{[\text{H}_3\text{O}^+][\text{HO}_2^-]}{[\text{H}_2\text{O}_2]}$$

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834 - x)} \quad \text{Assume } x \text{ is small compared to } 0.881834.$$

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834)}$$

$$[\text{H}_3\text{O}^+] = x = 1.2522567 \times 10^{-6} \text{ (unrounded)}$$

Check assumption:  $(1.2522567 \times 10^{-6} / 0.881834) \times 100\% = 0.0001\%$  error, so the assumption is valid.

$$M \text{ H}_3\text{PO}_4 = \left( \frac{1.00 \text{ g}}{\text{mL}} \right) \left( \frac{0.001\% \text{ H}_3\text{PO}_4}{100\%} \right) \left( \frac{1 \text{ mol H}_3\text{PO}_4}{97.99 \text{ g H}_3\text{PO}_4} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right)$$

$$= 1.0205 \times 10^{-4} M \text{ H}_3\text{PO}_4 \text{ (unrounded)}$$

From Appendix C,  $K_a$  for phosphoric acid is  $7.2 \times 10^{-3}$ . 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  $K_a$ .

	$\text{H}_3\text{PO}_4$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+$	+	$\text{H}_2\text{PO}_4^-$
Initial	$1.0205 \times 10^{-4}$		—		0		0
Change	— $x$		—		+ $x$		+ $x$
Equilibrium	$1.0205 \times 10^{-4}$		—		$x$		$x$

$$K_a = 7.2 \times 10^{-3} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$K_a = 7.2 \times 10^{-3} = \frac{[x][x]}{[1.0205 \times 10^{-4} - x]}$$

The problem will need to be solved as a quadratic.

$$x^2 = (7.2 \times 10^{-3})(1.0205 \times 10^{-4} - x) = 7.3476 \times 10^{-7} - 7.2 \times 10^{-3} x$$

$$x^2 + 7.2 \times 10^{-3} x - 7.3476 \times 10^{-7} = 0$$

$$a = 1 \quad b = 7.2 \times 10^{-3} \quad c = -7.3476 \times 10^{-7}$$

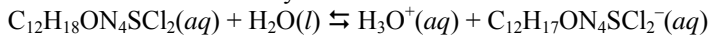
$$x = \frac{-7.2 \times 10^{-3} \pm \sqrt{(7.2 \times 10^{-3})^2 - 4(1)(-7.3476 \times 10^{-7})}}{2(1)}$$

$$x = 1.00643 \times 10^{-4} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

The concentration of hydronium ion produced by the phosphoric acid,  $1 \times 10^{-4} M$ , is greater than the concentration produced by the hydrogen peroxide,  $1 \times 10^{-6} M$ . Therefore, the **phosphoric acid** contributes more  $\text{H}_3\text{O}^+$  to the solution.

18.102 In step (1), the  $\text{RCOOH}$  is the Lewis base and the  $\text{H}^+$  is the Lewis acid. In step (2), the  $\text{RC(OH)}_2^+$  is the Lewis acid and the  $\text{R'OH}$  is the Lewis base.

18.103  $M$  is the unknown molarity of the thiamine.



$$\text{pH} = 3.50 \quad [\text{H}_3\text{O}^+] = 10^{-3.50} = 3.162 \times 10^{-4} M \text{ (unrounded)}$$

$$K_a = 3.37 \times 10^{-7} = \frac{[\text{H}_3\text{O}^+][\text{C}_{12}\text{H}_{17}\text{ON}_4\text{SCL}_2^-]}{[\text{C}_{12}\text{H}_{18}\text{ON}_4\text{SCL}_2]}$$

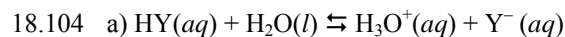
$$K_a = 3.37 \times 10^{-7} = \frac{(x)(x)}{(M - x)}$$

$$K_a = 3.37 \times 10^{-7} = \frac{(3.162 \times 10^{-4})(3.162 \times 10^{-4})}{(M - 3.162 \times 10^{-4})}$$

$$M = 0.296999998 M \text{ (unrounded)}$$

$$\text{Mass} = \left( \frac{0.296999998 \text{ mol Thiamine HCl}}{\text{L}} \right) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.00 \text{ mL}) \left( \frac{337.27 \text{ g Thiamine HCl}}{1 \text{ mol Thiamine HCl}} \right)$$

$$= 1.00169 = \mathbf{1.0 \text{ g thiamine hydrochloride}}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]}$$

Concentrations in Beaker A:

$$[\text{HY}] = (8 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.266667 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{Y}^-] = (4 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.133333 \text{ M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.133333][0.133333]}{[0.266667]} = 0.066667 = 0.067$$

Calculate the concentrations in Beakers B-D, then calculate Q to determine which are at equilibrium.

Concentrations in Beaker B:

$$[\text{HY}] = (6 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.20 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{Y}^-] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M}$$

$$Q = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.066667][0.066667]}{[0.20]} = 0.0222222 = 0.022$$

**Beaker B is not at equilibrium.**

Concentrations in Beaker C:

$$[\text{HY}] = (4 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.133333 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [\text{Y}^-] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M}$$

$$Q = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.066667][0.066667]}{[0.13333]} = 0.0333345 = 0.033$$

**Beaker C is not at equilibrium.**

Concentrations in Beaker D:

$$[\text{HY}] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M}$$

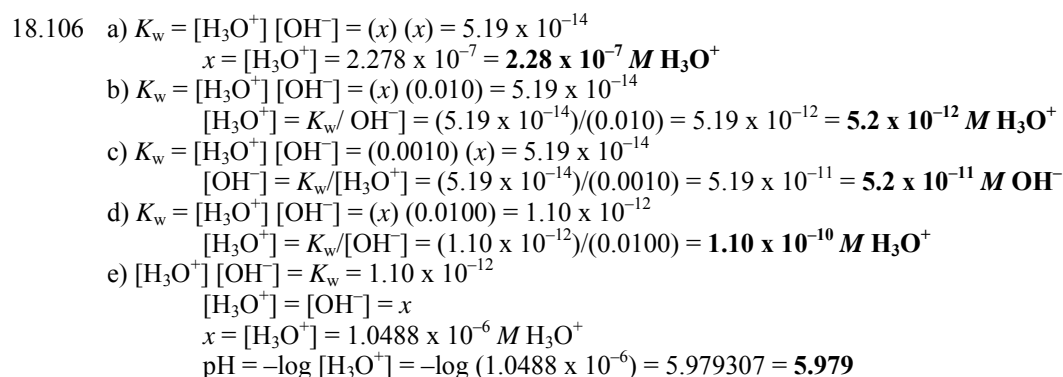
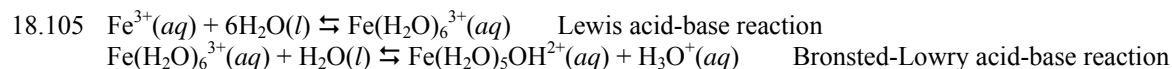
$$[\text{H}_3\text{O}^+] = [\text{Y}^-] = (2 \text{ particles}) \left( \frac{0.010 \text{ mol}}{1 \text{ particle}} \right) \left( \frac{1}{0.300 \text{ L}} \right) = 0.066667 \text{ M}$$

$$Q = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.066667][0.066667]}{[0.066667]} = 0.066667 = 0.067$$

**Beaker D is at equilibrium.**

b) For both beakers B and C,  $Q < K_a$ . 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.



18.107 The freezing point depression equation is required to determine the molality of the solution.

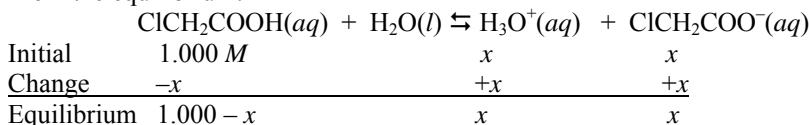
$$\Delta T = [0.00 - (-1.93^\circ\text{C})] = 1.93^\circ\text{C} = iK_f m$$

Temporarily assume  $i = 1$ .

$$m = \frac{\Delta T}{iK_f} = \frac{1.93^\circ\text{C}}{(1)(1.86^\circ\text{C}/m)} = 1.037634 m = 1.037634 M \text{ (unrounded)}$$

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:



The total concentration of all species is:

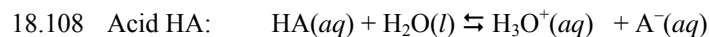
$$[\text{ClCH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{ClCH}_2\text{COO}^-] = 1.037634 M$$

$$[1.000 - x] + [x] + [x] = 1.000 + x = 1.037634 M$$

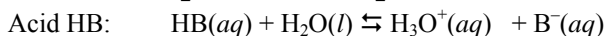
$$x = 0.037634 M \text{ (unrounded)}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_2\text{COO}^-]}{[\text{CH}_2\text{COOH}]}$$

$$K_a = \frac{(0.037634)(0.037634)}{(1.000 - 0.037634)} = 0.0014717 = \mathbf{0.00147}$$



$$K_a = \frac{\left[ \frac{0.010 \text{ mol}}{0.50 \text{ L}} \right] \left[ \frac{0.010 \text{ mol}}{0.50 \text{ L}} \right]}{\left[ \frac{0.050 \text{ mol}}{0.50 \text{ L}} \right]} = \mathbf{4.0 \times 10^{-3}}$$

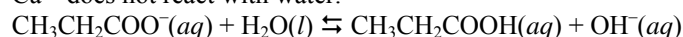


$$K_a = \frac{\left[ \frac{0.010 \text{ mol}}{0.25 \text{ L}} \right] \left[ \frac{0.010 \text{ mol}}{0.25 \text{ L}} \right]}{\left[ \frac{0.040 \text{ mol}}{0.25 \text{ L}} \right]} = \mathbf{1.0 \times 10^{-2}}$$

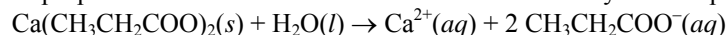
Acid **HB**, with the larger  $K_a$  value, is the stronger acid.

- 18.109 a) The two ions that comprise this salt are  $\text{Ca}^{2+}$  (derived from the strong base  $\text{Ca}(\text{OH})_2$ ) and  $\text{CH}_3\text{CH}_2\text{COO}^-$  (derived from the weak acid, propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ ). A salt derived from a strong base and weak acid produces a **basic** solution.

$\text{Ca}^{2+}$  does not react with water.



- b) Calcium propionate is a soluble salt and dissolves in water to yield two propionate ions:



The molarity of the solution is:

$$\text{Molarity} = \left( \frac{8.75 \text{ g Ca}(\text{CH}_3\text{CH}_2\text{COO})_2}{0.500 \text{ L}} \right) \left( \frac{1 \text{ mol Ca}(\text{CH}_3\text{CH}_2\text{COO})_2}{186.22 \text{ g Ca}(\text{CH}_3\text{CH}_2\text{COO})_2} \right) \left( \frac{2 \text{ mol CH}_3\text{CH}_2\text{COO}^-}{1 \text{ mol Ca}(\text{CH}_3\text{CH}_2\text{COO})_2} \right)$$

$$= 0.1879497 \text{ M CH}_3\text{CH}_2\text{COO}^- \text{ (unrounded)}$$

	$\text{CH}_3\text{CH}_2\text{COO}^-$	+	$\text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CH}_3\text{CH}_2\text{COOH}$	+	$\text{OH}^-$	
Initial	0.1879497 M				0		0	
Change	-x				+x		+x	
Equilibrium	0.1879497 - x				x		x	

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.3 \times 10^{-5}) = 7.6923 \times 10^{-10} \text{ (unrounded)}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{[\text{CH}_3\text{CH}_2\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.1879497 - x)} \quad \text{Assume } x \text{ is small compared to } 0.1879497.$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.1879497)}$$

$$x = 1.20239988 \times 10^{-5} = [\text{OH}^-] \text{ (unrounded)}$$

Check assumption:  $[1.20239988 \times 10^{-5}/0.1879497] \times 100\% = 0.006\%$ , therefore the assumption is good.

$$[\text{H}_3\text{O}^+] = K_w/[\text{OH}^-] = (1.0 \times 10^{-14})/(1.20239988 \times 10^{-5}) = 8.31671 \times 10^{-10} \text{ M H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.31671 \times 10^{-10}) = 9.0800 = \mathbf{9.08}$$

- 18.110  $\text{CO}_2(g) + 2 \text{H}_2\text{O}(l) \rightleftharpoons [\text{H}_2\text{CO}_3(aq)] + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)$

In an acidic solution (HCl), the equilibrium is shifted to the left, producing more gaseous  $\text{CO}_2$ . In an alkaline solution (NaOH), the  $\text{H}_3\text{O}^+$  formed is neutralized by the  $\text{OH}^-$ , shifting the equilibrium to the right and causing the solubility of  $\text{CO}_2$  to increase.

- 18.111 a)  $0^\circ\text{C} \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 1.139 \times 10^{-15}$

$$x = [\text{H}_3\text{O}^+] = 3.374907 \times 10^{-8} = \mathbf{3.375 \times 10^{-8} \text{ M H}_3\text{O}^+}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.374907 \times 10^{-8}) = 7.471730 = \mathbf{7.4717}$$

$$50^\circ\text{C} \quad K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 5.474 \times 10^{-14}$$

$$x = [\text{H}_3\text{O}^+] = 2.339658 \times 10^{-7} = \mathbf{2.340 \times 10^{-7} \text{ M H}_3\text{O}^+}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.339658 \times 10^{-7}) = 6.6308476 = \mathbf{6.6308}$$

- b)  $0^\circ\text{C} \quad K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 3.64 \times 10^{-16}$

$$x = [\text{D}_3\text{O}^+] = 1.907878 \times 10^{-8} = \mathbf{1.91 \times 10^{-8} \text{ M D}_3\text{O}^+}$$

$$\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (1.907878 \times 10^{-8}) = 7.719449 = \mathbf{7.719}$$

$$50^\circ\text{C} \quad K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 7.89 \times 10^{-15}$$

$$x = [\text{D}_3\text{O}^+] = 8.882567 \times 10^{-8} = \mathbf{8.88 \times 10^{-8} \text{ M D}_3\text{O}^+}$$

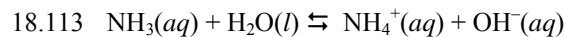
$$\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (8.882567 \times 10^{-8}) = 7.0514615 = \mathbf{7.051}$$

- 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.

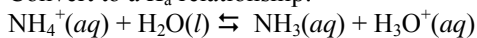
$$18.112 \text{ Molarity of HX} = \left( \frac{12.0 \text{ g HX}}{\text{L}} \right) \left( \frac{1 \text{ mol HX}}{150. \text{ g HX}} \right) = 0.0800 \text{ M HX}$$

$$\text{Molarity of HY} = \left( \frac{6.00 \text{ g HY}}{\text{L}} \right) \left( \frac{1 \text{ mol HY}}{50.0 \text{ g HY}} \right) = 0.120 \text{ M HY}$$

HX must be the stronger acid because lower concentration of HX has the same pH (it produces the same number of  $\text{H}^+$  ions) as a higher concentration of HY.



Convert to a  $K_a$  relationship:



$$K_a = K_w/K_b = (1.0 \times 10^{-14})/(1.76 \times 10^{-5}) = 5.6818 \times 10^{-10} \text{ (unrounded)}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+] + [\text{NH}_3]} = \frac{K_a}{[\text{H}_3\text{O}^+] + K_a}$$

$$\text{a) } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-7.00} = 1.0 \times 10^{-7} \text{ M H}_3\text{O}^+$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+] + [\text{NH}_3]} = \frac{5.6818 \times 10^{-10}}{1.0 \times 10^{-7} + 5.6818 \times 10^{-10}} = 5.6496995 \times 10^{-3} = \mathbf{5.6 \times 10^{-3}}$$

$$\text{b) } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10.00} = 1.0 \times 10^{-10} \text{ M H}_3\text{O}^+$$

$$\frac{[\text{NH}_3]}{[\text{NH}_4^+] + [\text{NH}_3]} = \frac{5.6818 \times 10^{-10}}{1.0 \times 10^{-10} + 5.6818 \times 10^{-10}} = 0.8503397 = \mathbf{0.85}$$

c) Increasing the pH shifts the equilibria towards  $\text{NH}_3$ . Ammonia is able to escape the solution as a gas.

18.114 a) As the pH of a water solution containing casein increases, the  $\text{H}^+$  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,  $-\text{NH}_2$  and  $=\text{NH}$  groups will accept  $\text{H}^+$  ions from solution. This will increase the number of charged groups, and the solubility of the histones will increase.

18.115 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  $[\text{H}_3\text{O}^+]$  concentration would shift the equilibrium to the right. More oxygen is absorbed, but it will be more difficult to remove the  $\text{O}_2$ .

d) An increase in the  $[\text{H}_3\text{O}^+]$  concentration would shift the equilibrium to the left. Less oxygen is absorbed, but it will be easier to remove the  $\text{O}_2$ .

18.116 a) There are 20  $\text{OH}^-$  ions for every 2  $\text{H}_3\text{O}^+$  ions; in other words,  $[\text{OH}^-] = 10 \times [\text{H}_3\text{O}^+]$

$$K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$1.0 \times 10^{-14} = [\text{H}_3\text{O}^+](10)[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 3.16 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.16 \times 10^{-8}) = \mathbf{7.5}$$

$$\text{b) For a pH of 4, } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4} = 1.0 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(1.0 \times 10^{-4}) = 1.0 \times 10^{-10} \text{ M OH}^-$$

$$[\text{H}_3\text{O}^+]/[\text{OH}^-] = 1.0 \times 10^{-4}/1.0 \times 10^{-10} = 1.0 \times 10^6$$

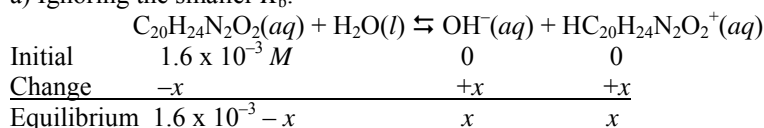
The  $\text{H}_3\text{O}^+$  concentration is 1 million times greater than that of  $\text{OH}^-$ . You would have to draw **one million**  $\text{H}_3\text{O}^+$  ions for every one  $\text{OH}^-$ .

18.117 Note that both  $pK_b$  values only have one significant figure. This will limit the final answers.

$$K_b (\text{tertiary amine N}) = 10^{-pK_b} = 10^{-5.1} = 7.94328 \times 10^{-6} \text{ (unrounded)}$$

$$K_b (\text{aromatic ring N}) = 10^{-pK_b} = 10^{-9.7} = 1.995262 \times 10^{-10} \text{ (unrounded)}$$

a) Ignoring the smaller  $K_b$ :



$$K_b = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]} = 7.94328 \times 10^{-6}$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3} - x]} = 7.94328 \times 10^{-6}$$

The problem will need to be solved as a quadratic.

$$x^2 = (7.94328 \times 10^{-6})(1.6 \times 10^{-3} - x) = 1.27092 \times 10^{-8} - 7.94328 \times 10^{-6} x$$

$$x^2 + 7.94328 \times 10^{-6} x - 1.27092 \times 10^{-8} = 0$$

$$a = 1 \quad b = 7.94328 \times 10^{-6} \quad c = -1.27092 \times 10^{-8}$$

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

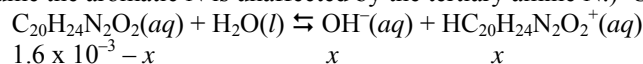
$$x = \frac{-7.94328 \times 10^{-6} \pm \sqrt{(7.94328 \times 10^{-6})^2 - 4(1)(-1.27092 \times 10^{-8})}}{2(1)}$$

$$x = 1.08833 \times 10^{-4} M \text{ OH}^- \text{ (unrounded)}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.08833 \times 10^{-4}} = 9.18838955 \times 10^{-11} M \text{ H}_3\text{O}^+ \text{ (unrounded)}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.18838955 \times 10^{-11}) = 10.03676 = \mathbf{10.0}$$

b) (Assume the aromatic N is unaffected by the tertiary amine N.) Use the  $K_b$  value for the aromatic nitrogen.



$$K_b = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]} = 1.995262 \times 10^{-10}$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3} - x]} = 1.995262 \times 10^{-10} \quad \text{Assume } x \text{ is small compared to } 1.6 \times 10^{-3}.$$

$$K_b = \frac{[x][x]}{[1.6 \times 10^{-3}]} = 1.995262 \times 10^{-10}$$

$$x = 5.6501 \times 10^{-7} M \text{ OH}^- \text{ (unrounded)}$$

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)  $\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7.94328 \times 10^{-6}} = 1.2589 \times 10^{-9} \text{ (unrounded)}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.33 - x)} \quad \text{Assume } x \text{ is small compared to } 0.33.$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.33)}$$

$$[\text{H}_3\text{O}^+] = x = 2.038248 \times 10^{-5} \text{ (unrounded)}$$

Check assumption:  $(2.038248 \times 10^{-5}/0.33) \times 100\% = 0.006\%$ . The assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.038248 \times 10^{-5}) = 4.69074 = \mathbf{4.7}$$

d) Quinine hydrochloride will be indicated as QHCl.

$$M = \left( \frac{1.5\%}{100\%} \right) \left( \frac{1.0 \text{ g}}{\text{mL}} \right) \left( \frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left( \frac{1 \text{ mol QHCl}}{360.87 \text{ QHCl}} \right) = 0.041566 \text{ M (unrounded)}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.041566 - x)} \quad \text{Assume } x \text{ is small compared to } 0.041566.$$

$$K_a = 1.2589 \times 10^{-9} = \frac{(x)(x)}{(0.041566)}$$

$$[\text{H}_3\text{O}^+] = x = 7.23377 \times 10^{-6} \text{ (unrounded)}$$

Check assumption:  $(7.23377 \times 10^{-6}/0.041566) \times 100\% = 0.02\%$ . The assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.23377 \times 10^{-6}) = 5.1406 = \mathbf{5.1}$$

18.118 a) Annual depositions:

$$(\text{NH}_4)_2\text{SO}_4: \left( \frac{3.0 (\text{NH}_4)_2\text{SO}_4}{9.5 \text{ total}} \right) (2.688 \text{ g/m}^2) = 0.8488421 = 0.85 \text{ g/m}^2$$

$$\text{NH}_4\text{HSO}_4: \left( \frac{5.5 \text{ NH}_4\text{HSO}_4}{9.5 \text{ total}} \right) (2.688 \text{ g/m}^2) = 1.55621 = 1.56 \text{ g/m}^2$$

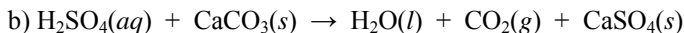
$$\text{H}_2\text{SO}_4: \left( \frac{1.0 \text{ H}_2\text{SO}_4}{9.5 \text{ total}} \right) (2.688 \text{ g/m}^2) = 0.282947 = 0.28 \text{ g/m}^2$$

$(\text{NH}_4)_2\text{SO}_4$  is a weak acid;  $\text{NH}_4\text{HSO}_4$  has half the acidity per mole as  $\text{H}_2\text{SO}_4$  so the equivalent amount of sulfuric acid deposition would be:

$$\left( \frac{1.56 \text{ g NH}_4\text{HSO}_4}{\text{m}^2} \right) \left( \frac{0.50 \text{ M NH}_4\text{HSO}_4}{1 \text{ M H}_2\text{SO}_4} \right) \left( \frac{98.1 \text{ g H}_2\text{SO}_4}{115.1 \text{ g NH}_4\text{HSO}_4} \right) = 0.664796 \text{ g/m}^2$$

$$\text{Total as sulfuric acid} = 0.66 \text{ g/m}^2 + 0.28 \text{ g/m}^2 = 0.94 \text{ g/m}^2$$

$$\left( \frac{0.94 \text{ g H}_2\text{SO}_4}{\text{m}^2} \right) (10. \text{ km}^2) \left( \frac{1000 \text{ m}}{1 \text{ km}} \right)^2 \left( \frac{1 \text{ kg}}{1000 \text{ g}} \right) = \mathbf{9.4 \times 10^3 \text{ kg}}$$



There is a 1:1 mole ratio between  $\text{H}_2\text{SO}_4$  and  $\text{CaCO}_3$ .

$$\begin{aligned} (9.4 \times 10^3 \text{ kg H}_2\text{SO}_4) \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} \right) \left( \frac{1 \text{ mol CaCO}_3}{1 \text{ mol H}_2\text{SO}_4} \right) \left( \frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3} \right) \left( \frac{2.205 \text{ lb}}{1000 \text{ g}} \right) \\ = 2.1150 \times 10^4 = \mathbf{2.1 \times 10^4 \text{ lb CaCO}_3} \end{aligned}$$

$$\text{c) Moles of H}^+ = (9.4 \times 10^3 \text{ kg H}_2\text{SO}_4) \left( \frac{1000 \text{ g}}{1 \text{ kg}} \right) \left( \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} \right) \left( \frac{2 \text{ mol H}^+}{1 \text{ mol H}_2\text{SO}_4} \right) = 1.91641 \times 10^5 \text{ mol H}^+$$

$$\text{Volume of lake} = (10. \text{ km}^2) \left( \frac{1000 \text{ m}}{1 \text{ km}} \right)^2 (3 \text{ m}) \left( \frac{1 \text{ L}}{10^{-3} \text{ m}^3} \right) = 3.0 \times 10^{10} \text{ L}$$

$$\text{Molarity of H}^+ = \frac{1.91641 \times 10^5 \text{ mol H}^+}{3.0 \times 10^{10} \text{ L}} = 6.3880 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (6.3880 \times 10^{-6}) = 5.1946 = \mathbf{5.19}$$



18.119 a) At pH = 7.00,  $[H_3O^+] = 10^{-pH} = 10^{-7.00} = 1.0 \times 10^{-7} M$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{K_a}{[H_3O^+] + K_a}$$
$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{2.9 \times 10^{-8}}{1.0 \times 10^{-7} + 2.9 \times 10^{-8}} = 0.224806 = \mathbf{0.22}$$

b) At pH = 10.00,  $[H_3O^+] = 10^{-pH} = 10^{-10.00} = 1.0 \times 10^{-10} M$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{K_a}{[H_3O^+] + K_a}$$
$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{2.9 \times 10^{-8}}{1.0 \times 10^{-10} + 2.9 \times 10^{-8}} = 0.99656 = \mathbf{1.0}$$

18.120 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 =  $(2/8) \times 100\% = \mathbf{25\%}$

e) **NaY**, the weakest base, will give the highest pOH and the smallest pH this is.