

CHAPTER 16 ACID-BASE EQUILIBRIA

END-OF-CHAPTER PROBLEMS

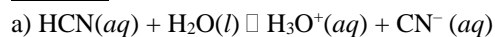
- 16.2 (a) All Arrhenius acids contain hydrogen and produce hydronium ion (H_3O^+) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous solution.
(b) Neutralization occurs when each H_3O^+ molecule combines with an OH^- molecule to form two molecules of H_2O . Chemists found that the $\Delta_r H$ 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.
- 16.4 (a) 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.
(b) Ammonia, NH_3 , and carbonate ion, CO_3^{2-} , are two Brønsted-Lowry bases that are not Arrhenius bases because they do not contain hydroxide ions. Brønsted-Lowry acids must contain an ionizable H atom in order to be proton donors, so a Brønsted-Lowry acid that is not an Arrhenius acid cannot be identified. (Other examples are also acceptable.)
- 16.7 An amphoteric substance can act as either an acid or a base. In the presence of a strong base (OH^-), the dihydrogen phosphate ion acts like an acid by donating hydrogen:
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{aq}) + \text{HPO}_4^{2-}(\text{aq})$
In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:
 $\text{H}_2\text{PO}_4^-(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{H}_3\text{PO}_4(\text{aq}) + \text{Cl}^-(\text{aq})$
- 16.8 (a) Strong acids and bases dissociate completely into their ions when dissolved in water. Weak acids and bases only partially dissociate.
(b) The characteristic property of all weak acids and bases is that a significant number of the 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. The same is true for bases. A strong base dissociates to produce the same concentration of OH^- ion as that of the strong base. The concentration of OH^- that results from dissociation of a weak base is much less than the concentration of the original base.
- 16.9 Plan: Recall that an Arrhenius acid contains hydrogen and produces hydrogen ion (H^+) (hydronium ion, H_3O^+) in aqueous solution.
Solution:
a) Water, H_2O , is an **Arrhenius acid** because it produces H_3O^+ ion in aqueous solution. Water is also an Arrhenius base because it produces the OH^- ion as well.
b) Calcium hydroxide, $\text{Ca}(\text{OH})_2$ is a base, not an acid.
c) Phosphorous acid, H_3PO_3 , is a weak **Arrhenius acid**. It is weak because the number of O atoms equals the number of ionizable H atoms.
d) Hydroiodic acid, HI, is a strong **Arrhenius acid**.
- 16.11 Plan: All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous solution.
Solution:
Barium hydroxide, $\text{Ba}(\text{OH})_2$, and potassium hydroxide, KOH, (**b and d**) are Arrhenius bases because they contain hydroxide ions and form OH^- when dissolved in water. H_3AsO_4 and HClO , (a) and (c), are Arrhenius acids, not bases.

16.13 Plan: K_a is the equilibrium constant for an acid dissociation which has the generic equation

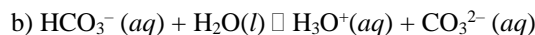
$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$. The K_a expression is $\frac{[H_3O^+][A^-]}{[HA]}$. $H_2O(l)$ has an activity of 1 and

thus does not appear in the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

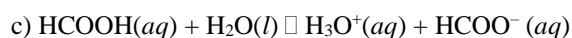
Solution:



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



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



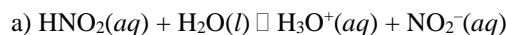
$$K_a = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

16.15 Plan: K_a is the equilibrium constant for an acid dissociation which has the generic equation

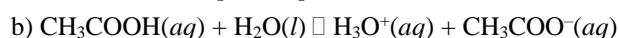
$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$. The K_a expression is $\frac{[H_3O^+][A^-]}{[HA]}$. $H_2O(l)$ has an activity of 1 and

thus does not appear in the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

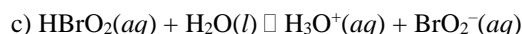
Solution:



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



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



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

16.17 Plan: K_a is the equilibrium constant for an acid dissociation which has the generic equation

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$. The K_a expression is $\frac{[H_3O^+][A^-]}{[HA]}$. $H_2O(l)$ has an activity of 1 and

thus does not appear in the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

Solution:

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



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

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



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

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



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

- 16.19 Plan: To derive the conjugate base, remove one H from the acid and decrease the charge by 1 (acids donate H^+). Since each formula in this problem is neutral, the conjugate base will have a charge of -1 .

Solution:

a) Cl^- b) HCO_3^- c) OH^-

- 16.21 Plan: To derive the conjugate acid, add an H and increase the charge by 1 (bases accept H^+).

Solution:

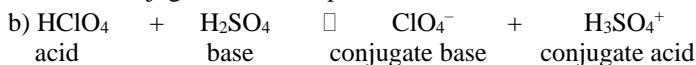
a) NH_4^+ b) NH_3 c) $\text{C}_{10}\text{H}_{14}\text{N}_2\text{H}^+$

- 16.23 Plan: The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:

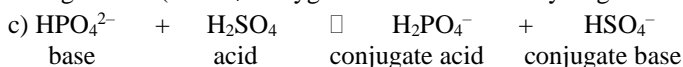


Conjugate acid-base pairs: HCl/Cl^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$



Conjugate acid-base pairs: $\text{HClO}_4/\text{ClO}_4^-$ and $\text{H}_3\text{SO}_4^+/\text{H}_2\text{SO}_4$

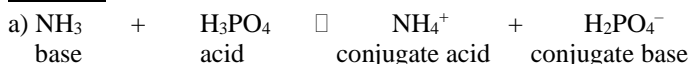
Note: Perchloric acid is able to protonate another strong acid, H_2SO_4 , because perchloric acid is a stronger acid. (HClO_4 's oxygen atoms exceed its hydrogen atoms by one more than H_2SO_4 .)



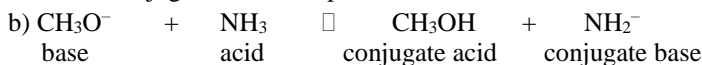
Conjugate acid-base pairs: $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$

- 16.25 Plan: The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

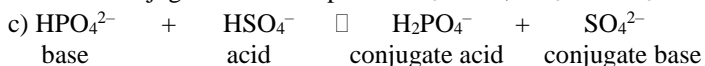
Solution:



Conjugate acid-base pairs: $\text{H}_3\text{PO}_4/\text{H}_2\text{PO}_4^-$; $\text{NH}_4^+/\text{NH}_3$



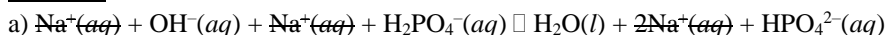
Conjugate acid-base pairs: $\text{NH}_3/\text{NH}_2^-$; $\text{CH}_3\text{OH}/\text{CH}_3\text{O}^-$

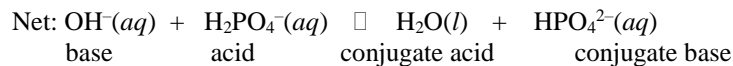


Conjugate acid-base pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}$; $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$

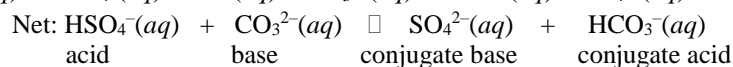
- 16.27 Plan: Write total ionic equations (show all soluble ionic substances as dissociated into ions) and then remove the spectator ions to write the net ionic equations. The (aq) subscript denotes that each species is soluble and dissociates in water. The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:





Conjugate acid-base pairs: $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{H}_2\text{O}/\text{OH}^-$

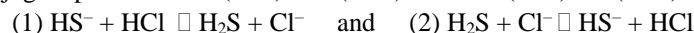


Conjugate acid-base pairs: $\text{HSO}_4^-/\text{SO}_4^{2-}$ and $\text{HCO}_3^-/\text{CO}_3^{2-}$

- 16.29 Plan: The two possible reactions involve reacting the acid from one conjugate pair with the base from the other conjugate pair. The reaction that favors the products ($K > 1$) is the one in which the stronger acid produces the weaker acid. The reaction that favors reactants ($K < 1$) is the reaction in which the weaker acid produces the stronger acid.

Solution:

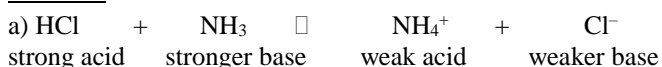
The conjugate pairs are H_2S (acid)/ HS^- (base) and HCl (acid)/ Cl^- (base). Two reactions are possible:



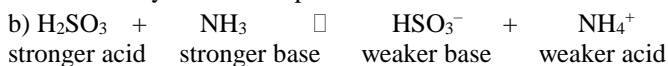
The first reaction is the reverse of the second. HCl is a strong acid and H_2S a weak acid. Reaction (1) with the stronger acid producing the weaker acid favors products and $K > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K < 1$.

- 16.31 Plan: An acid-base reaction that favors the products ($K > 1$) is one in which the stronger acid produces the weaker acid. Use the figure to decide which of the two acids is the stronger acid.

Solution:



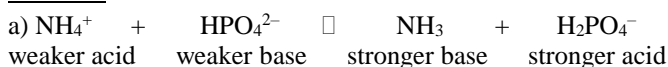
HCl is ranked above NH_4^+ in the list of conjugate acid-base pair strength and is the stronger acid. NH_3 is ranked above Cl^- and is the stronger base. NH_3 is shown as a “stronger” base because it is stronger than Cl^- , but is not considered a “strong” base. The reaction proceeds toward the production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



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

- 16.33 Plan: An acid-base reaction that favors the reactants ($K < 1$) is one in which the weaker acid produces the stronger acid. Use the figure to decide which of the two acids is the weaker acid.

Solution:



$K < 1$ The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.



$K < 1$ The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.

- 16.35 Plan: K_a values are listed in the Appendix. The larger the K_a value, the stronger the acid. The K_a value for hydroiodic acid, HI, is not shown because K_a approaches infinity for strong acids and is not meaningful.

Solution:

HI is the strongest acid (it is one of the six strong acids), and acetic acid, CH_3COOH , is the weakest:



- 16.37 Plan: Strong acids are the hydrohalic acids HCl, HBr, HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more; these include HNO_3 , H_2SO_4 , and HClO_4 . All other acids are weak acids. Strong bases are metal hydroxides (or oxides) in which the metal is a Group 1 metal or Ca, Sr, or Ba in Group 2. Weak bases are NH_3 and amines.

Solution:

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

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

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

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

- 16.39 Plan: Strong acids are the hydrohalic acids HCl, HBr, HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more; these include HNO_3 , H_2SO_4 , and HClO_4 . All other acids are weak acids. Strong bases are metal hydroxides (or oxides) in which the metal is a Group 1 metal or Ca, Sr, or Ba in Group 2. Weak bases are NH_3 and amines.

Solution:

a) Rubidium hydroxide, RbOH , is a **strong base** because Rb is a Group 1 metal.

b) Hydrobromic acid, HBr, is a **strong acid**, because it is one of the listed hydrohalic acids.

c) Hydrogen telluride, H_2Te , is a **weak acid**, because H is not bonded to an oxygen or halide.

d) Hypochlorous acid, HClO , is a **weak acid**. The number of O atoms is one, which is equal to the number of ionizable H atoms identifying HClO as a weak acid.

- 16.44 Plan: The lower the concentration of hydrogen (H^+) ions, the higher the pH. pH increases as K_a or the concentration (mol/L) of acid decreases. Recall that $\text{p}K_a = -\log K_a$.

Solution:

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 $[\text{H}^+]$ and higher pH.

c) **Lower concentration** of the same acid means lower concentration of hydrogen ions produced. The 0.01 mol/L solution has a lower $[\text{H}^+]$ and higher pH.

d) At the same concentration, strong acids dissociate to produce more hydrogen ions than weak acids. The 0.1 mol/L solution of a **weak acid** has a lower $[\text{H}^+]$ and higher pH.

e) Bases produce OH^- ions in solution, so the concentration of hydrogen ion for a solution of a base solution is lower than that for a solution of an acid. The 0.01 mol/L **base solution** has the higher pH.

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

- 16.45 Plan: Part a) can be approached two ways. Because NaOH is a strong base, the $[\text{OH}^-]_{\text{eq}} = [\text{NaOH}]_{\text{init}}$. One method involves calculating $[\text{H}^+]$ using $K_w = [\text{H}^+][\text{OH}^-]$, then calculating pH from the relationship $\text{pH} = -\log [\text{H}^+]$. The other method involves calculating pOH and then using $\text{pH} + \text{pOH} = 14.00$ to calculate pH. Part b) also has two acceptable methods analogous to those in part a); only one method will be shown.
- Solution:
- a) First method:
 $K_w = [\text{H}^+][\text{OH}^-]$
- $$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.0111} = 9.0090 \times 10^{-13} \text{ mol/L}$$
- $$\text{pH} = -\log [\text{H}^+] = -\log (9.0090 \times 10^{-13}) = 12.04532 = \mathbf{12.05}$$
- Second method:
 $\text{pOH} = -\log [\text{OH}^-] = -\log (0.0111) = 1.954677$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.954677 = 12.04532 = \mathbf{12.05}$
 With a $\text{pH} > 7$, the solution is **basic**.
- b) For a strong acid such as HCl:
 $[\text{H}^+] = [\text{HCl}] = 1.35 \times 10^{-3} \text{ mol/L}$
 $\text{pH} = -\log (1.35 \times 10^{-3}) = 2.869666$
 $\text{pOH} = 14.00 - 2.869666 = 11.130334 = \mathbf{11.13}$ With a $\text{pH} < 7$, the solution is **acidic**.
- 16.47 Plan: HI is a strong acid, so $[\text{H}^+] = [\text{HI}]$ and the pH can be calculated from the relationship $\text{pH} = -\log [\text{H}_3\text{O}^+]$. $\text{Ba}(\text{OH})_2$ is a strong base, so $[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2]$ and $\text{pOH} = -\log [\text{OH}^-]$.
- Solution:
- a) $[\text{H}^+] = [\text{HI}] = 6.14 \times 10^{-3} \text{ mol/L}$.
 $\text{pH} = -\log (6.14 \times 10^{-3}) = 2.211832 = \mathbf{2.212}$. Solution is **acidic**.
- b) $[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2] = 2(2.55 \text{ M}) = 5.10 \text{ mol/L}$
 $\text{pOH} = -\log (5.10) = -0.70757 = \mathbf{-0.708}$. Solution is **basic**.
- 16.49 Plan: The relationships are: $\text{pH} = -\log [\text{H}^+]$ and $[\text{H}^+] = 10^{-\text{pH}}$; $\text{pOH} = -\log [\text{OH}^-]$ and $[\text{OH}^-] = 10^{-\text{pOH}}$; and $14 = \text{pH} + \text{pOH}$.
- Solution:
- a) $[\text{H}^+] = 10^{-\text{pH}} = 10^{-9.85} = 1.4125375 \times 10^{-10} = \mathbf{1.4 \times 10^{-10} \text{ mol/L H}^+}$
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.85 = \mathbf{4.15}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.15} = 7.0794578 \times 10^{-5} = \mathbf{7.1 \times 10^{-5} \text{ mol/L OH}^-}$
- b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.43 = \mathbf{4.57}$
 $[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.57} = 2.691535 \times 10^{-5} = \mathbf{2.7 \times 10^{-5} \text{ mol/L H}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.43} = 3.7153523 \times 10^{-10} = \mathbf{3.7 \times 10^{-10} \text{ mol/L OH}^-}$
- 16.51 Plan: The relationships are: $\text{pH} = -\log [\text{H}^+]$ and $[\text{H}^+] = 10^{-\text{pH}}$; $\text{pOH} = -\log [\text{OH}^-]$ and $[\text{OH}^-] = 10^{-\text{pOH}}$; and $14 = \text{pH} + \text{pOH}$.
- Solution:
- a) $[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.77} = 1.69824 \times 10^{-5} = \mathbf{1.7 \times 10^{-5} \text{ mol/L H}^+}$
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 4.77 = \mathbf{9.23}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.23} = 5.8884 \times 10^{-10} = \mathbf{5.9 \times 10^{-10} \text{ mol/L OH}^-}$
- b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.65 = \mathbf{8.35}$
 $[\text{H}^+] = 10^{-\text{pH}} = 10^{-8.35} = 4.46684 \times 10^{-9} = \mathbf{4.5 \times 10^{-9} \text{ mol/L H}_3\text{O}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.65} = 2.23872 \times 10^{-6} = \mathbf{2.2 \times 10^{-6} \text{ mol/L OH}^-}$
- 16.53 Plan: The pH is increasing, so the solution is becoming more basic. Therefore, OH^- ion is added to increase the pH. Since one mole of H_3O^+ will react with one mole of OH^- , the difference in $[\text{H}^+]$ would be equal to the $[\text{OH}^-]$ added. Use the relationship $[\text{H}^+] = 10^{-\text{pH}}$ to find $[\text{H}^+]$ at each pH.
- Solution:
- $$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.15} = 7.07946 \times 10^{-4} \text{ mol/L H}^+$$
- $$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.65} = 2.23872 \times 10^{-4} \text{ mol/L H}^+$$
- $$\text{Add } (7.07946 \times 10^{-4} \text{ mol/L} - 2.23872 \times 10^{-4} \text{ mol/L}) = 4.84074 \times 10^{-4} = \mathbf{4.8 \times 10^{-4} \text{ mol of OH}^- \text{ per litre}}$$

- 16.55 Plan: The pH is increasing, so the solution is becoming more basic. Therefore, OH^- ion is added to increase the pH. Since one mole of H^+ will react with one mole of OH^- , the difference in $[\text{H}^+]$ would be equal to the $[\text{OH}^-]$ added. Use the relationship $[\text{H}^+] = 10^{-\text{pH}}$ to find $[\text{H}^+]$ at each pH.

Solution:

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-4.52} = 3.01995 \times 10^{-5} \text{ mol/L } \text{H}^+$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-5.25} = 5.623413 \times 10^{-6} \text{ mol/L } \text{H}^+$$

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

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

- 16.58 Plan: Apply Le Chatelier's principle in part a). In part b), given that the pH is 6.80, $[\text{H}^+]$ can be calculated by using the relationship $[\text{H}^+] = 10^{-\text{pH}}$. The problem specifies that the solution is neutral (pure water), meaning $[\text{H}^+] = [\text{OH}^-]$. A new K_w can then be calculated.

Solution:

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 .

$$\text{b) } [\text{H}^+] = 10^{-\text{pH}} = 10^{-6.80} = 1.58489 \times 10^{-7} \text{ mol/L } \text{H}^+ = \mathbf{1.6 \times 10^{-7} \text{ mol/L } } [\text{H}^+] = [\text{OH}^-]$$

$$K_w = [\text{H}^+][\text{OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = \mathbf{2.5 \times 10^{-14}}$$

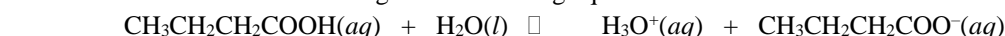
For a neutral solution: $\text{pH} = \mathbf{pOH = 6.80}$

- 16.70 a) The concentration of a strong acid is **very different** before and after dissociation since a strong acid exhibits 100% dissociation. After dissociation, the concentration of the strong acid approaches 0, or $[\text{HA}] \approx 0$.
 b) A weak acid dissociates to a very small extent ($\ll 100\%$), so the acid concentration after dissociation is **nearly the same** as before dissociation.
 c) Same as b), but the percent, or extent, of dissociation is greater than in b).
 d) Same as a)
- 16.71 **No**, HCl and CH_3COOH are never of equal strength because HCl is a strong acid with $K_a > 1$ and CH_3COOH is a weak acid with $K_a < 1$. The K_a of the acid, not the concentration of H_3O^+ in a solution of the acid, determines the strength of the acid.

- 16.74 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table and substitute the given value of $[\text{H}_3\text{O}^+]$ for x ; solve for K_a .

Solution:

Butanoic acid dissociates according to the following equation:



Initial: 0.15 mol/L

0

0

Change: -x

+x

+x

Equilibrium: 0.15 - x

x

x

According to the information given in the problem, $[\text{H}_3\text{O}^+]_{\text{eq}} = 1.51 \times 10^{-3} \text{ mol/L} = x$

Thus, $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-] = 1.51 \times 10^{-3} \text{ mol/L}$

$[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}] = (0.15 - x) = (0.15 - 1.51 \times 10^{-3}) \text{ mol/L} = 0.14849 \text{ mol/L}$

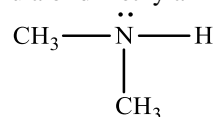
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-]}{[\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}]}$$

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

- 16.76 Plan: Write the balanced equation for the base reaction and the expression for K_b . Set up a reaction table in which x = the concentration of reacted base and also $[\text{OH}^-]$. Use the expression for K_b to solve for x , $[\text{OH}^-]$, and then calculate $[\text{H}^+]$ and pH.

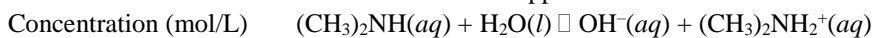
Solution:

The formula of dimethylamine has two methyl (CH_3) 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.



Initial 0.070 0 0

Change -x +x +x

Equilibrium 0.070 - x x x

$$K_b = 5.9 \times 10^{-4} = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]}$$

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

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

$$x = 6.4265 \times 10^{-3} \text{ mol/L}$$

Check assumption that x is small compared to 0.070:

$$\frac{6.4265 \times 10^{-3}}{0.070} (100\%) = 9\% \text{ error, so the assumption is not valid.}$$

The problem will need to be solved as a quadratic.

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

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

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

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

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

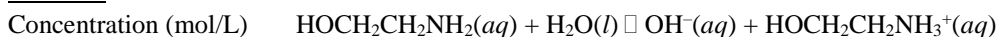
$$x = \frac{-5.9 \times 10^{-4} \pm \sqrt{(5.9 \times 10^{-4})^2 - 4(1)(-4.13 \times 10^{-5})}}{2(1)} = 6.13827 \times 10^{-3} \text{ mol/L OH}^-$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.13827 \times 10^{-3}} = 1.629124 \times 10^{-12} \text{ mol/L H}^+$$

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

- 16.78 Plan: Write the balanced equation for the base reaction and the expression for K_b . Set up a reaction table in which x = the concentration of reacted base and also $[\text{OH}^-]$. Use the expression for K_b to solve for x , $[\text{OH}^-]$, and then calculate $[\text{H}_3\text{O}^+]$ and pH.

Solution:



Initial 0.25 0 0

Change -x +x +x

Equilibrium 0.25 - x x x

$$K_b = 3.2 \times 10^{-5} = \frac{[\text{HOCH}_2\text{CH}_2\text{NH}_3^+][\text{OH}^-]}{[\text{HOCH}_2\text{CH}_2\text{NH}_2]}$$

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

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

$$x = 2.8284 \times 10^{-3} \text{ mol/L OH}^-$$

Check assumption that x is small compared to 0.25:

$$\frac{2.8284 \times 10^{-3}}{0.25} (100\%) = 1\% \text{ error, so the assumption is valid.}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.8284 \times 10^{-3}} = 3.535568 \times 10^{-12} \text{ mol/L H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log (3.535568 \times 10^{-12}) = 11.4515 = \mathbf{11.45}$$

- 16.80 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated HNO_2 and also $[\text{H}_3\text{O}^+]$. Use the expression for K_a to solve for x ($[\text{H}^+]$).

Solution:

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

Concentration (mol/L)	$\text{HNO}_2(aq)$	+	$\text{H}_2\text{O}(l)$	\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 H_3O^+ contribution from water has been neglected.)

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

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

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

$$x = 0.020639767$$

Check assumption that x is small compared to 0.60:

$$\frac{0.020639767}{0.60} (100\%) = 3.4\% \text{ error, so the assumption is valid.}$$

$$[\text{H}^+] = [\text{NO}_2^-] = \mathbf{2.1 \times 10^{-2} \text{ mol/L}}$$

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 $K_w = 1.0 \times 10^{-14}$

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

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

- 16.82 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated acid and also $[\text{H}_3\text{O}^+]$. Use the expression for K_a to solve for x ($[\text{H}^+]$). K_a is found from the $\text{p}K_a$ by using the relationship $K_a = 10^{-\text{p}K_a}$.

Solution:

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

Concentration (mol/L) $\text{ClCH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClCH}_2\text{COO}^-(aq)$

Initial	1.25	0	0
---------	------	---	---

Change	-x	+x	+x
Equilibrium	1.25 - x	x	x

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

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

Assume x is small compared to 1.25.

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

$$x = 0.04106337$$

Check assumption that x is small compared to 1.25:

$$\frac{0.04106337}{1.25}(100\%) = 3.3\%. \text{ The assumption is good.}$$

$$[\text{H}^+] = [\text{ClCH}_2\text{COO}^-] = \mathbf{0.041 \text{ mol/L}}$$

$$[\text{ClCH}_2\text{COOH}] = 1.25 - 0.04106337 = 1.20894 = \mathbf{1.21 \text{ mol/L}}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (0.04106337) = 1.3865 = \mathbf{1.39}$$

- 16.84 Plan: In part a), potassium cyanide, when placed in water, dissociates into potassium ions, K^+ , and cyanide ions, CN^- . Potassium ion is the conjugate acid of a strong base, KOH, so K^+ does not react with water. Cyanide ion is the conjugate base of a weak acid, HCN, so it does react with a base-dissociation reaction. To find the pH first set up a reaction table and use K_b for CN^- to calculate $[\text{OH}^-]$. Find the K_b for CN^- from the equation $K_w = K_a \times K_b$. In part b), the salt triethylammonium chloride in water dissociates into two ions: $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ and Cl^- . Chloride ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Triethylammonium ion is the conjugate acid of a weak base, so an acid-dissociation reaction determines the pH of the solution. To find the pH first set up a reaction table and use K_a for $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ to calculate $[\text{H}^+]$. Find the K_a for $(\text{CH}_3\text{CH}_2)_3\text{NH}^+$ from the equation $K_w = K_a \times K_b$.

Solution:



Concentration (mol/L)	$\text{CN}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCN}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.150		—		0		0
Change	-x				+x		+x
Equilibrium	0.150 - x				x		x

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

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

$$K_b = 1.612903 \times 10^{-5} = \frac{[x][x]}{[0.150 - x]}$$

Assume x is small compared to 0.150.

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

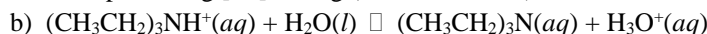
$$x = 1.555 \times 10^{-3} \text{ mol/L } \text{OH}^-$$

Check assumption that x is small compared to 0.150:

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

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.555 \times 10^{-3}} = 6.430868 \times 10^{-12} \text{ mol/L } \text{H}^+$$

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



Concentration (mol/L)	$(\text{CH}_3\text{CH}_2)_3\text{NH}^+(aq) + \text{H}_2\text{O}(l)$	\rightleftharpoons	$(\text{CH}_3\text{CH}_2)_3\text{N}(aq) + \text{H}_3\text{O}^+(aq)$
Initial	0.40	—	0
Change	-x		+x
Equilibrium	0.40 - x		x

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

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

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

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

$$[\text{H}^+] = x = 2.7735 \times 10^{-6} \text{ mol/L}$$

Check assumption that x is small compared to 0.40:

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

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

- 16.86 Plan: In part a), potassium formate, when placed in water, dissociates into potassium ions, K^+ , and formate ions, HCOO^- . Potassium ion is the conjugate acid of a strong base, KOH, so K^+ does not react with water. Formate ion is the conjugate base of a weak acid, HCOOH, so it does react with a base-dissociation reaction. To find the pH first set up a reaction table and use K_b for HCOO^- to calculate $[\text{OH}^-]$. Find the K_b for HCOO^- from the equation $K_w = K_a \times K_b$. In part b), the salt ammonium bromide in water dissociates into two ions: NH_4^+ and Br^- . Bromide ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Ammonium ion is the conjugate acid of the weak base NH_3 , so an acid-dissociation reaction determines the pH of the solution. To find the pH first set up a reaction table and use K_a for NH_4^+ to calculate $[\text{H}_3\text{O}^+]$. Find the K_a for NH_4^+ from the equation $K_w = K_a \times K_b$.

Solution:



Concentration (mol/L)	$\text{HCOO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCOOH}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.65		—		0		0
Change	-x				+x		+x
Equilibrium	0.65 - x				x		x

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

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

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

$$K_b = 5.55556 \times 10^{-11} = \frac{(x)(x)}{(0.65)}$$

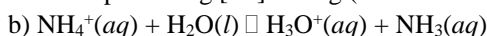
$$x = 6.00925 \times 10^{-6} \text{ mol/L } \text{OH}^-$$

Check assumption that x is small compared to 0.65:

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

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.00925 \times 10^{-6}} = 1.66410 \times 10^{-9} \text{ mol/L H}^+$$

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



Concentration (mol/L)	$\text{NH}_4^+(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{NH}_3(aq)$	+	$\text{H}_3\text{O}^+(aq)$
Initial	0.85		—		0		0
Change	-x				+x		+x
Equilibrium	$0.85 - x$				x		x

$$K_a \text{ of } \text{NH}_4^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.681818 \times 10^{-10}$$

$$K_a = 5.681818 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$$

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

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

$$[\text{H}^+] = x = 2.1976 \times 10^{-5} \text{ mol/L}$$

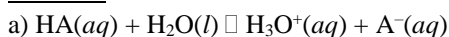
Check assumption that x is small compared to 0.85:

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

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

- 16.88 Plan: Write the acid-dissociation reaction and the expression for K_a . 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, which also equals $[\text{H}_3\text{O}^+]$. HA will be used as the formula of the acid. Set up a reaction table in which x = the concentration of the dissociated acid and $[\text{H}_3\text{O}^+]$. pH and $[\text{OH}^-]$ are determined from $[\text{H}_3\text{O}^+]$. Substitute $[\text{HA}]$, $[\text{A}^-]$, and $[\text{H}_3\text{O}^+]$ into the expression for K_a to find the value of K_a .

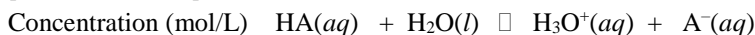
Solution:



$$\text{Percent HA} = \frac{\text{dissociated acid}}{\text{initial acid}} (100\%)$$

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

$$[\text{Dissociated acid}] = x = 6.0 \times 10^{-3} \text{ mol/L}$$



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

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

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

$$[\text{Dissociated acid}] = x = [\text{A}^-] = [\text{H}_3\text{O}^+] = \mathbf{6.0 \times 10^{-3} \text{ mol/L}}$$

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

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-3}} = 1.6666667 \times 10^{-12} = \mathbf{1.7 \times 10^{-12} \text{ mol/L}}$$

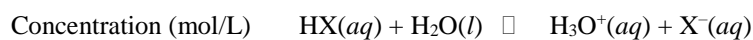
$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.6666667 \times 10^{-12}) = 11.7782 = \mathbf{11.78}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.0 \times 10^{-3})(6.0 \times 10^{-3})}{(0.20 - 6.0 \times 10^{-3})} = 1.85567 \times 10^{-4} = \mathbf{1.9 \times 10^{-4}}$$

- 16.90 Plan: Write the acid-dissociation reaction and the expression for K_a . Calculate the concentration (mol/L) of HX by dividing moles by volume. Convert pH to $[\text{H}_3\text{O}^+]$, set up a reaction table in which x = the concentration of the dissociated acid and also $[\text{H}_3\text{O}^+]$, and substitute into the equilibrium expression to find K_a .

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



$$\text{Initial:} \quad 0.381679 \quad 0 \quad 0$$

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

$$\text{Equilibrium:} \quad 0.381679 - x \quad x \quad x$$

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-3.54} = 2.88403 \times 10^{-4} \text{ mol/L} = x$$

$$\text{Thus, } [\text{H}^+] = [\text{X}^-] = 2.88403 \times 10^{-4} \text{ mol/L, and } [\text{HX}] = (0.381679 - 2.88403 \times 10^{-4}) \text{ mol/L}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]} = \frac{(2.88403 \times 10^{-4})(2.88403 \times 10^{-4})}{(0.381679 - 2.88403 \times 10^{-4})} = 2.18087 \times 10^{-7} = \mathbf{2.2 \times 10^{-7}}$$

- 16.92 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated acid and also $[\text{H}_3\text{O}^+]$. Use the expression for K_a to solve for x ($[\text{H}^+]$). OH^- and then pOH can be found from $[\text{H}^+]$.

Solution:



$$\text{Initial} \quad 0.075 \quad - \quad 0 \quad 0$$

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

$$\text{Equilibrium} \quad 0.075 - x \quad x \quad x$$

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

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

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

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

$$[\text{H}^+] = x = 4.3732 \times 10^{-3}$$

Check assumption that x is small compared to 0.075:

$$\frac{4.3732 \times 10^{-3}}{0.075} (100\%) = 6\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.075, and it is necessary to use the quadratic equation.

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

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

$$a = 1$$

$$b = 2.55 \times 10^{-4}$$

$$c = -1.9125 \times 10^{-5}$$

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

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

$$x = 0.00425 \text{ or } -0.004503$$

(The -0.004503 value is not possible.)

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

b) Concentration (mol/L)	$\text{HZ}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Z}^-(aq)$
Initial	0.045		—		0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.045 - x$				x		x

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

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

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

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

$$[\text{H}^+] = x = 3.3875 \times 10^{-3}$$

Check assumption that x is small compared to 0.045 :

$$\frac{3.3875 \times 10^{-3}}{0.045} (100\%) = 7.5\% \text{ error, so the assumption is not valid.}$$

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.

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

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

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

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

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

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

$$x = 3.26238 \times 10^{-3} \text{ mol/L } \text{H}^+$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{3.26238 \times 10^{-3}} = 3.0652468 \times 10^{-12} \text{ mol/L}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (3.0652468 \times 10^{-12}) = 11.51353 = \mathbf{11.51}$$

- 16.94 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated acid and also $[\text{H}^+]$. Use the expression for K_a to solve for x ($[\text{H}^+]$). OH^- and then pOH can be found from $[\text{H}^+]$.

Solution:

a) Concentration (mol/L)	$\text{HY}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Y}^-(aq)$
Initial	0.175		—		0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.175 - x$				x		x

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

$$K_a = 1.50 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]}$$

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

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

$$[\text{H}^+] = x = 5.1235 \times 10^{-3} \text{ mol/L}$$

Check assumption that x is small compared to 0.175:

$$\frac{5.1235 \times 10^{-3}}{0.175} (100\%) = 3\% \text{ error, so the assumption is valid.}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (5.1235 \times 10^{-3}) = 2.29043 = \mathbf{2.290}$$

b) Concentration (mol/L)	HX(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	X ⁻ (aq)
Initial	0.175		—		0		0
Change	-x				+x		+x
Equilibrium	0.175 - x				x		x

(The H₃O⁺ contribution from water has been neglected.)

$$K_a = 2.00 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{X}^-]}{[\text{HX}]}$$

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

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

$$[\text{H}^+] = x = 5.9161 \times 10^{-2} \text{ mol/L}$$

Check assumption that x is small compared to 0.175:

$$\frac{5.9161 \times 10^{-2}}{0.175} (100\%) = 34\% \text{ error, so the assumption is not valid.}$$

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

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

$$x^2 = (2.00 \times 10^{-2})(0.175 - x) = 0.0035 - 2.00 \times 10^{-2}x$$

$$x^2 + 2.00 \times 10^{-2}x - 0.0035 = 0$$

$$a = 1 \quad b = 2.00 \times 10^{-2} \quad c = -0.0035$$

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

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

$$x = 5.00 \times 10^{-2} \text{ mol/L H}^+$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{5.00 \times 10^{-2}} = 2.00 \times 10^{-13} \text{ mol/L}$$

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

- 16.96 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated acid and also $[H_3O^+]$. Use the expression for K_a to solve for x , the concentration of benzoate ion at equilibrium. Then use the initial concentration of benzoic acid and the equilibrium concentration of benzoate to find % dissociation.

Solution:

Concentration (mol/L)	$C_6H_5COOH(aq)$	+	$H_2O(l)$	\rightleftharpoons	$H_3O^+(aq)$	+	$C_6H_5COO^-(aq)$
Initial	0.55		—		0		0
Change	-x				+x		+x
Equilibrium	$0.55 - x$				x		x

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

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

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

$$x = 5.8864 \times 10^{-3} \text{ mol/L}$$

$$\text{Percent } C_6H_5COOH \text{ dissociated} = \frac{[C_6H_5COOH]_{\text{dissociated}}}{[C_6H_5COOH]_{\text{initial}}} (100)$$

$$\text{Percent } C_6H_5COOH \text{ dissociated} = \frac{5.8864 \times 10^{-3} \text{ mol/L}}{0.55 \text{ mol/L}} (100\%) = 1.07025 = \mathbf{1.1\%}$$

- 16.98 Plan: Write balanced chemical equations and corresponding equilibrium expressions for dissociation of hydrosulfuric acid, H_2S , and HS^- . Since $K_{a_1} \gg K_{a_2}$, assume that almost all of the H_3O^+ comes from the first dissociation. Set up reaction tables in which x = the concentration of dissociated acid and $[H_3O^+]$.

Solution:



$$K_{a_1} = 9 \times 10^{-8} = \frac{[H_3O^+][HS^-]}{[H_2S]}$$



$$K_{a_2} = 1 \times 10^{-17} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

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

$$K_{a_1} = 9 \times 10^{-8} = \frac{[H_3O^+][HS^-]}{[H_2S]}$$

$$K_{a_1} = 9 \times 10^{-8} = \frac{[x][x]}{[0.10 - x]} \quad \text{Assume } x \text{ is small compared to } 0.10.$$

$$K_{a_1} = 9 \times 10^{-8} = \frac{[x][x]}{[0.10]}$$

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

$$[H^+] = [HS^-] = x = \mathbf{9 \times 10^{-5} \text{ mol/L}}$$

$$\text{pH} = -\log [H^+] = -\log (9.48683 \times 10^{-5}) = 4.022878 = \mathbf{4.0}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{9.48683 \times 10^{-5}} = 1.05409 \times 10^{-10} = \mathbf{1 \times 10^{-10} \text{ mol/L}}$$

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

$$[\text{H}_2\text{S}] = 0.10 - x = 0.10 - 9.48683 \times 10^{-5} = 0.099905 = \mathbf{0.10 \text{ mol/L}}$$

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

Calculate $[\text{S}^{2-}]$ by using the K_{a_2} expression and assuming that $[\text{HS}^-]$ and $[\text{H}_3\text{O}^+]$ come mostly from the first dissociation. This new calculation will have a new x value.

Concentration (mol/L)	$\text{HS}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{S}^{2-}(aq)$
Initial	9.48683×10^{-5}		—		9.48683×10^{-5}		0
Change	$-x$				$+x$		$+x$
Equilibrium	$9.48683 \times 10^{-5} - x$				$9.48683 \times 10^{-5} + x$		x

$$K_{a_2} = 1 \times 10^{-17} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

$$K_{a_2} = 1 \times 10^{-17} = \frac{(9.48683 \times 10^{-5} + x)(x)}{(9.48683 \times 10^{-5} - x)} \quad \text{Assume } x \text{ is small compared to } 9.48683 \times 10^{-5}.$$

$$K_{a_2} = 1 \times 10^{-17} = \frac{(9.48683 \times 10^{-5})(x)}{(9.48683 \times 10^{-5})}$$

$$x = [\text{S}^{2-}] = \mathbf{1 \times 10^{-17} \text{ mol/L}}$$

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

- 16.101 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table in which x = the concentration of the dissociated acid and also $[\text{H}_3\text{O}^+]$. Use the expression for K_a to solve for x , the concentration of formate ion at equilibrium. Then use the initial concentration of formic acid and the equilibrium concentration of formate to find % dissociation.

Solution:

Concentration (mol/L)	$\text{HCOOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{HCOO}^-(aq)$
Initial	0.75				0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.75 - x$				x		x

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

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

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

$$x = 1.161895 \times 10^{-2}$$

$$\text{Percent HCOOH dissociated} = \frac{[\text{HCOOH}]_{\text{dissociated}}}{[\text{HCOOH}]_{\text{initial}}} (100\%)$$

$$\text{Percent HCOOH dissociated} = \frac{1.161895 \times 10^{-2} \text{ mol/L}}{0.75 \text{ mol/L}} (100\%) = 1.54919 \% = \mathbf{1.5\%}$$

- 16.102 Plan: First, calculate the initial concentration (mol/L) of ClO^- from the mass percent. Then, set up reaction table with base dissociation of ClO^- . Find the K_b for ClO^- from the equation $K_w = K_a \times K_b$, using the K_a for HClO from Appendix C.

Solution:

Concentration (mol/L) of $\text{ClO}^- =$

$$\left(\frac{1 \text{ mL solution}}{10^{-3} \text{ L solution}} \right) \left(\frac{1.0 \text{ g solution}}{1 \text{ mL solution}} \right) \left(\frac{6.5\% \text{ NaClO}}{100\% \text{ Solution}} \right) \left(\frac{1 \text{ mol NaClO}}{74.44 \text{ g NaClO}} \right) \left(\frac{1 \text{ mol ClO}^-}{1 \text{ mol NaClO}} \right)$$

$$= 0.873186 \text{ mol/L ClO}^-$$

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

Concentration (mol/L)	$\text{ClO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HClO}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.873186		—		0		0
Change	—x				+x		+x
Equilibrium	0.873186 — x				x		x

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

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

$$K_b = 3.448275862 \times 10^{-7} = \frac{[x][x]}{[0.873186 - x]}$$

Assume x is small compared to 0.873186.

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

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

Check assumption that x is small compared to 0.873186:

$$\frac{5.4872 \times 10^{-4}}{0.873186} (100\%) = 0.006\% \text{ error, so the assumption is valid.}$$

$$[\text{H}]^+ = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.4872 \times 10^{-4}} = 1.82242 \times 10^{-11} \text{ mol/L H}^+$$

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

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

- 16.107 The two factors that explain the greater acid strength of HClO_4 are:

- 1) Chlorine is more electronegative than iodine, so chlorine more strongly attracts the electrons in the bond with oxygen. This makes the H in HClO_4 less tightly held by the oxygen than the H in HIO .
- 2) Perchloric acid has more oxygen atoms than HIO , which leads to a greater shift in electron density from the hydrogen atom to the oxygen atoms making the H in HClO_4 more susceptible to transfer to a base.

- 16.108 Plan: For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal down a column.

Solution:

- a) Selenic acid, H_2SeO_4 , is the stronger acid because it contains more oxygen atoms.
- b) Phosphoric acid, H_3PO_4 , is the stronger acid because P is more electronegative than As.
- c) Hydrotelluric acid, H_2Te , is the stronger acid because Te is larger than S and so the Te–H bond is weaker.

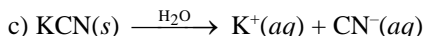
- 16.110 Plan: For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal in a column.
Solution:
 a) **H₂Se**, hydrogen selenide, is a stronger acid than H₃As, arsenic hydride, because Se is more electronegative than As.
 b) **B(OH)₃**, boric acid also written as H₃BO₃, is a stronger acid than Al(OH)₃, aluminum hydroxide, because boron is more electronegative than aluminum.
 c) **HBrO₂**, bromous acid, is a stronger acid than HBrO, hypobromous acid, because there are more oxygen atoms in HBrO₂ than in HBrO.
- 16.112 Plan: 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.
Solution:
 a) Copper(II) bromide, CuBr₂, contains Cu²⁺ ion with $K_a = 3 \times 10^{-8}$. Aluminum bromide, AlBr₃, contains Al³⁺ ion with $K_a = 1 \times 10^{-5}$. The concentrations of Cu²⁺ and Al³⁺ are equal, but the K_a of AlBr₃ is almost three orders of magnitude greater. Therefore, **0.5 mol/L AlBr₃** is the stronger acid and would have the lower pH.
 b) Zinc chloride, ZnCl₂, contains the Zn²⁺ ion with $K_a = 1 \times 10^{-9}$. Tin(II) chloride, SnCl₂, contains the Sn²⁺ ion with $K_a = 4 \times 10^{-4}$. Since both solutions have the same concentration, and K_a (Sn²⁺) > K_a (Zn²⁺), **0.3 mol/L SnCl₂** is the stronger acid and would have the lower pH.
- 16.114 Plan: A higher pH (more basic solution) results when an acid has a smaller K_a (from the Appendix). Determine the ion formed from each salt and compare the corresponding K_a values from Appendix C.
Solution:
 a) The **Ni(NO₃)₂** solution has a higher pH than the Co(NO₃)₂ solution because K_a of Ni²⁺ (1×10^{-10}) is smaller than the K_a of Co²⁺ (2×10^{-10}). Note that nitrate ion is the conjugate base of a strong acid and therefore does not influence the pH of the solution.
 b) The **Al(NO₃)₃** solution has a higher pH than the Cr(NO₃)₂ solution because K_a of Al³⁺ (1×10^{-5}) is smaller than the K_a of Cr³⁺ (1×10^{-4}).
- 16.117 Sodium fluoride, NaF, contains the cation of a strong base, NaOH, and anion of a weak acid, HF.
 This combination yields a salt that is basic in aqueous solution as the F⁻ ion acts as a base:

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

 Sodium chloride, NaCl, is the salt of a strong base, NaOH, and strong acid, HCl. This combination yields a salt that is neutral in aqueous solution as neither Na⁺ or Cl⁻ react in water to change the [H₃O⁺].
- 16.119 Plan: 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.
Solution:
 a) $KBr(s) \xrightarrow{H_2O} K^+(aq) + Br^-(aq)$
 K^+ is the conjugate acid of a strong base, so it does not influence pH.
 Br^- is the conjugate base of a strong acid, so it does not influence pH.
 Since neither ion influences the pH of the solution, it will remain at the **neutral** pH of pure water.
 b) $NH_4I(s) \xrightarrow{H_2O} NH_4^+(aq) + I^-(aq)$
 NH_4^+ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H₃O⁺ as represented by the acid-dissociation reaction:

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

 I^- is the conjugate base of a strong acid, so it will not influence the pH.
 The production of H₃O⁺ from the ammonium ion makes the solution of NH₄I **acidic**.



K^+ is the conjugate acid of a strong base, so it does not influence pH.

CN^- is the conjugate base of a weak acid, so it will act as a weak base in solution and impact pH by the base-dissociation reaction:

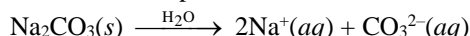


Hydroxide ions are produced in this equilibrium so solution will be **basic**.

- 16.121 Plan: 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.

Solution:

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



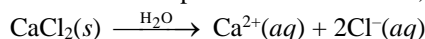
Sodium ion is derived from the strong base NaOH . Carbonate ion is derived from the weak acid HCO_3^- .

A salt derived from a strong base and a weak acid produces a **basic** solution.

Na^+ does not react with water.



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

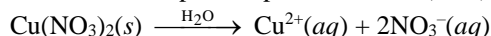


Calcium ion is derived from the strong base $\text{Ca}(\text{OH})_2$. Chloride ion is derived from the strong acid HCl .

A salt derived from a strong base and strong acid produces a **neutral** solution.

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

- c) The two ions that comprise cupric nitrate, $\text{Cu}(\text{NO}_3)_2$, are the cupric ion, Cu^{2+} , and the nitrate ion, NO_3^- .



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



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

- 16.123 Plan: 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.

Solution:

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

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



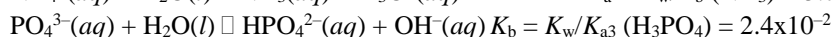
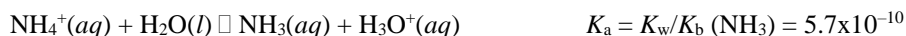
- c) A solution of dimethylammonium bromide is **acidic** because $(\text{CH}_3)_2\text{NH}_2^+$ is the conjugate acid of a weak base and therefore forms H_3O^+ in solution whereas Br^- is the conjugate base of a strong acid and does not influence the pH of the solution. The acid-dissociation reaction for methylammonium ion is



- 16.125 Plan: 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.

Solution:

- a) The two ions that comprise ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$, are the ammonium ion, NH_4^+ , and the phosphate ion, PO_4^{3-} .



A comparison of K_a and K_b is necessary since both ions are derived from a weak base and weak acid.

The K_a of NH_4^+ is determined by using the K_b of its conjugate base, NH_3 (Appendix). The K_b of PO_4^{3-}

is determined by using the K_a of its conjugate acid, HPO_4^{2-} . The K_a of HPO_4^{2-} comes from K_{a3} of H_3PO_4 (Appendix). Since $K_b > K_a$, a solution of $(\text{NH}_4)_3\text{PO}_4$ is **basic**.

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



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

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



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

- 16.127 Plan: 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. Use K_a and K_b values to rank the pH; the larger the K_a value, the lower the pH and the larger the K_b value, the higher the pH.

Solution:

a) Order of increasing pH: **$\text{Fe}(\text{NO}_3)_2 < \text{KNO}_3 < \text{K}_2\text{SO}_3 < \text{K}_2\text{S}$** (assuming concentrations equivalent)

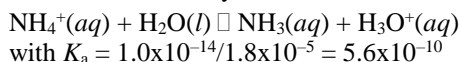
Iron(II) nitrate, $\text{Fe}(\text{NO}_3)_2$, is an acidic solution because the iron ion is a small, highly charged metal ion that acts as a weak acid and nitrate ion is the conjugate base of a strong acid, so it does not influence pH.

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

Potassium sulfite, K_2SO_3 , and potassium sulfide, K_2S , are similar in that the potassium ion does not influence solution pH, but the anions do because they are conjugate bases of weak acids. K_a for HSO_3^- is 6.5×10^{-8} , so K_b for SO_3^{2-} is 1.5×10^{-7} , which indicates that sulfite ion is a weak base. K_a for HS^- is 1×10^{-17} (see the table of K_a values for polyprotic acids), so sulfide ion has a K_b equal to 1×10^3 . Sulfide ion is thus a strong base. The solution of a strong base will have a greater concentration of hydroxide ions (and higher pH) than a solution of a weak base of equivalent concentrations.

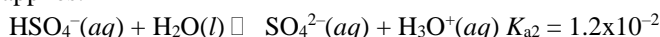
b) In order of increasing pH: **$\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$**

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

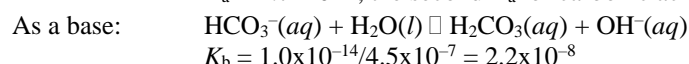
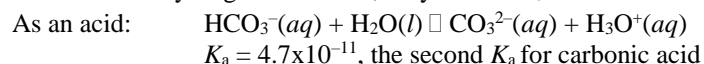


Therefore, the solution of ammonium nitrate is acidic.

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

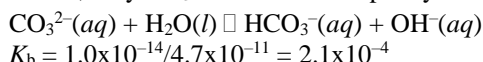


In solutions of sodium hydrogen carbonate, only the HCO_3^- will influence pH and it, like HSO_4^- , is amphoteric:



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

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



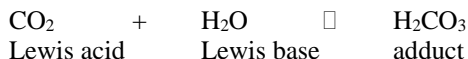
Therefore, the solution of sodium carbonate is basic.

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

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

- 16.129 (a) Both methoxide ion and amide ion produce OH^- in aqueous solution. In water, the strongest base possible is OH^- . Since both bases produce OH^- in water, both bases appear equally strong.
- (b) $\text{CH}_3\text{O}^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^-(aq) + \text{CH}_3\text{OH}(aq)$
 $\text{NH}_2^-(aq) + \text{H}_2\text{O}(l) \rightarrow \text{OH}^-(aq) + \text{NH}_3(aq)$
- 16.131 Ammonia, NH_3 , is a more basic solvent than H_2O . In a more basic solvent, weak acids like HF act like strong acids and are 100% dissociated.
- 16.133 A Lewis acid is defined as an electron-pair acceptor, while a Brønsted-Lowry acid is a proton donor. If only the proton in a Brønsted-Lowry acid is considered, then every Brønsted-Lowry acid fits the definition of a Lewis acid since the proton is accepting an electron pair when it bonds with a base. There are Lewis acids that do not include a proton, so all Lewis acids are not Brønsted-Lowry acids.
 A Lewis base is defined as an electron-pair donor and a Brønsted-Lowry base is a proton acceptor. In this case, the two definitions are essentially the same.
- 16.134 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, water molecules solvate metal ions very well:
 $\text{Ni}^{2+}(aq) + 4\text{H}_2\text{O}(l) \rightleftharpoons \text{Ni}(\text{H}_2\text{O})_4^{2+}(aq)$
 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**.
- 16.137 Plan: A Lewis acid is an electron-pair acceptor and therefore must be able to accept an electron pair. A Lewis base is an electron-pair donor and therefore must have an electron pair to donate.
Solution:
 a) Cu^{2+} is a **Lewis acid** because it accepts electron pairs from molecules such as water.
 b) Cl^- is a **Lewis base** because it has lone pairs of electrons it can donate to a Lewis acid.
 c) Tin(II) chloride, SnCl_2 , is a compound with a structure similar to carbon dioxide, so it will act as a **Lewis acid** to form an additional bond to the tin.
 d) Oxygen difluoride, OF_2 , is a **Lewis base** with a structure similar to water, where the oxygen has lone pairs of electrons that it can donate to a Lewis acid.
- 16.139 Plan: A Lewis acid is an electron-pair acceptor and therefore must be able to accept an electron pair. A Lewis base is an electron-pair donor and therefore must have an electron pair to donate.
Solution:
 a) The boron atom in boron trifluoride, BF_3 , is electron deficient (has six electrons instead of eight) and can accept an electron pair; it is a **Lewis acid**.
 b) The sulfide ion, S^{2-} , can donate any of four electron pairs and is a **Lewis base**.
 c) The Lewis dot structure for the sulfite ion, SO_3^{2-} , shows lone pairs on the sulfur and on the oxygen atoms. The sulfur atom has a lone electron pair that it can donate more easily than the electronegative oxygen in the formation of an adduct. The sulfite ion is a **Lewis base**.
 d) Sulfur trioxide, SO_3 , acts as a **Lewis acid**.
- 16.141 Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.
Solution:
 a) Sodium ion is the Lewis acid because it is accepting electron pairs from water, the Lewis base.
- $$\begin{array}{ccccccc} \text{Na}^+ & + & 6\text{H}_2\text{O} & \rightleftharpoons & \text{Na}(\text{H}_2\text{O})_6^+ \\ \text{Lewis acid} & & \text{Lewis base} & & \text{adduct} \end{array}$$

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



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



- 16.143 Plan: In an Arrhenius acid-base reaction, H^+ ions react with OH^- ions to produce H_2O . In a Brønsted-Lowry acid-base reaction, an acid donates H^+ to a base. In a Lewis acid-base reaction, an electron pair is donated by the base and accepted by the acid.

Solution:

a) Since neither H^+ nor OH^- is involved, this is not an Arrhenius acid-base reaction. Since there is no exchange of protons, this is not a Brønsted-Lowry reaction. This reaction is only classified as **Lewis acid-base reaction**, where Ag^+ is the acid and NH_3 is the base.

b) Again, no OH^- is involved, so this is not an Arrhenius acid-base reaction. This is an exchange of a proton, from H_2SO_4 to NH_3 , so it is a **Brønsted-Lowry acid-base reaction**. Since the Lewis definition is most inclusive, anything that is classified as a Brønsted-Lowry (or Arrhenius) reaction is automatically classified as a **Lewis acid-base reaction**.

c) This is not an acid-base reaction.

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

- 16.146 Plan: Calculate the $[\text{H}^+]$ using the pH values given. Determine the value of K_w from the $\text{p}K_w$ given. The $[\text{H}^+]$ is combined with the K_w value at 37°C to find $[\text{OH}^-]$ using $K_w = [\text{H}^+][\text{OH}^-]$.

Solution:

$$K_w = 10^{-\text{p}K_w} = 10^{-13.63} = 2.34423 \times 10^{-14}$$

$$K_w = [\text{H}^+][\text{OH}^-] = 2.34423 \times 10^{-14} \text{ at } 37^\circ\text{C}$$

$[\text{H}^+]$ range

$$\text{High value (low pH)} = 10^{-\text{pH}} = 10^{-7.35} = 4.46684 \times 10^{-8} = 4.5 \times 10^{-8} \text{ mol/L } \text{H}^+$$

$$\text{Low value (high pH)} = 10^{-\text{pH}} = 10^{-7.45} = 3.54813 \times 10^{-8} = 3.5 \times 10^{-8} \text{ mol/L } \text{H}^+$$

$$\text{Range: } \mathbf{3.5 \times 10^{-8} \text{ to } 4.5 \times 10^{-8} \text{ mol/L } \text{H}^+}$$

$[\text{OH}^-]$ range

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.34423 \times 10^{-14} \text{ at } 37^\circ\text{C}$$

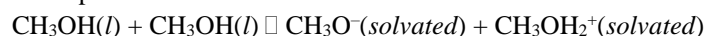
$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}$$

$$\text{High value (high pH)} = \frac{2.34423 \times 10^{-14}}{3.54813 \times 10^{-8}} = 6.60695 \times 10^{-7} = 6.6 \times 10^{-7} \text{ mol/L } \text{OH}^-$$

$$\text{Low value (low pH)} = \frac{2.34423 \times 10^{-14}}{4.46684 \times 10^{-8}} = 5.24807 \times 10^{-7} = 5.2 \times 10^{-7} \text{ mol/L } \text{OH}^-$$

$$\text{Range: } \mathbf{5.2 \times 10^{-7} \text{ to } 6.6 \times 10^{-7} \text{ mol/L } \text{OH}^-}$$

- 16.147 a) Acids will vary in the amount they dissociate (acid strength) depending on the acid-base character of the solvent. Water and methanol have different acid-base characters.
 b) The K_a is the measure of an acid's strength. A stronger acid has a smaller pK_a . Therefore, phenol is a stronger acid in water than it is in methanol. In other words, water more readily accepts a proton from phenol than does methanol, i.e., methanol is a weaker base than water.
 c) $C_6H_5OH(solvent) + CH_3OH(l) \rightleftharpoons CH_3OH_2^+(solvent) + C_6H_5O^-(solvent)$
 The term "*solvated*" is analogous to "*aqueous*." "*Aqueous*" would be incorrect in this case because the reaction does not take place in water.
 d) In the autoionization process, one methanol molecule is the proton donor while another methanol molecule is the proton acceptor.



In this equation "*(solvated)*" indicates that the molecules are solvated by methanol.

The equilibrium constant for this reaction is the autoionization constant of methanol:

$$K = [CH_3O^-][CH_3OH_2^+]$$

- 16.150 Plan: A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor. Recall that n is the main energy level and l is the orbital type.

Solution:

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.

- 16.151 Plan: A 10-fold dilution means that the chemist takes 1 mL of the 1.0×10^{-5} mol/L 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. $c_1V_1 = c_2V_2$ can be used to find the concentration (mol/L) after each dilution. After each dilution, find $[H^+]$ and calculate the pH.

Solution:

Hydrochloric acid is a strong acid that completely dissociates in water. Therefore, the concentration of H^+ is the same as the starting acid concentration: $[H^+] = [HCl]$. The original solution pH:

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

Dilution 1: $c_1V_1 = c_2V_2$

$$(1.0 \times 10^{-5} \text{ mol/L})(1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[H^+]_{HCl} = 1.0 \times 10^{-6} \text{ mol/L } H^+$$

$$pH = -\log(1.0 \times 10^{-6}) = \mathbf{6.00}$$

Dilution 2:

$$(1.0 \times 10^{-6} \text{ mol/L})(1.0 \text{ mL}) = (x)(10. \text{ mL})$$

$$[H^+]_{HCl} = 1.0 \times 10^{-7} \text{ mol/L } H^+$$

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 1.0×10^{-7} mol/L. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (mol/L)	$2H_2O(l)$	\rightleftharpoons	$H_3O^+(aq)$	+	$OH^-(aq)$
Initial	—		1×10^{-7}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-7} + x$		x

$$K_w = [H^+][OH^-] = (1 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-7}x - 1.0 \times 10^{-14} = 0$

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

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

$$x = 6.18034 \times 10^{-8}$$

$$[\text{H}^+] = (1.0 \times 10^{-7} + x) \text{ mol/L} = (1.0 \times 10^{-7} + 6.18034 \times 10^{-8}) \text{ mol/L} = 1.618034 \times 10^{-7} \text{ mol/L H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.618034 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$$

Dilution 3:

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

$$[\text{H}^+]_{\text{HCl}} = 1.0 \times 10^{-8} \text{ mol/L H}^+$$

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

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

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

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

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

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

$$x = 9.51249 \times 10^{-8}$$

$$[\text{H}^+] = (1.0 \times 10^{-8} + x) \text{ mol/L} = (1.0 \times 10^{-8} + 9.51249 \times 10^{-8}) \text{ mol/L} = 1.051249 \times 10^{-7} \text{ mol/L H}^+$$

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

Dilution 4:

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

$$[\text{H}^+]_{\text{HCl}} = 1.0 \times 10^{-9} \text{ mol/L H}^+$$

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

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

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

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

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

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

$$x = 9.95012 \times 10^{-8}$$

$$[\text{H}^+] = (1.0 \times 10^{-9} + x) \text{ mol/L} = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) \text{ mol/L} = 1.005012 \times 10^{-7} \text{ mol/L H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1.005012 \times 10^{-7}) = 6.9978 = \mathbf{7.00}$$

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.

- 16.157 Plan: Determine the hydrogen ion concentration from the pH. The concentration (mol/L) and the volume will give the number of moles, and with the aid of Avogadro's number, the number of ions may be found.

Solution:

$$c \text{ H}^+ = 10^{-\text{pH}} = 10^{-6.2} = 6.30957 \times 10^{-7} \text{ mol/L}$$

$$\left(\frac{6.30957 \times 10^{-7} \text{ mol H}_3\text{O}^+}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left(\frac{1250. \text{ mL}}{\text{d}} \right) \left(\frac{7 \text{ d}}{1 \text{ wk}} \right) \left(\frac{6.022 \times 10^{23} \text{ H}_3\text{O}^+}{1 \text{ mol H}_3\text{O}^+} \right) = 3.32467 \times 10^{18} = \mathbf{3 \times 10^{18} \text{ H}^+}$$

The pH has only one significant figure, and limits the significant figures in the final answer.

- 16.160 Plan: Determine K_b using the relationship $K_b = 10^{-\text{p}K_b}$. Write the base-dissociation equation and set up a reaction table in which x = the amount of OH^- produced. Use the K_b expression to find x . From $[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$ and then pH can be calculated.

Solution:

$$K_b = 10^{\text{p}K_b} = 10^{-5.91} = 1.23027 \times 10^{-6}$$

	TRIS(aq)	+	H ₂ O(l)	⇌	OH ⁻ (aq)	+	HTRIS ⁺ (aq)
Initial	0.075		—		0		0
Change	-x				+x		+x
Equilibrium	0.075 - x				x		x

$$K_b = 1.23027 \times 10^{-6} = \frac{[\text{HTRIS}^+][\text{OH}^-]}{[\text{TRIS}]}$$

$$K_b = 1.23027 \times 10^{-6} = \frac{[x][x]}{[0.075 - x]} \quad \text{Assume } x \text{ is small compared to } 0.075.$$

$$K_b = 1.23027 \times 10^{-6} = \frac{[x][x]}{[0.075]}$$

$$x = [\text{OH}^-] = 3.03760 \times 10^{-4} \text{ mol/L OH}^-$$

Check assumption that x is small compared to 0.075:

$$\frac{3.03760 \times 10^{-4}}{0.075} (100\%) = 0.40\% \text{ error, so the assumption is valid.}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.03760 \times 10^{-4}} = 3.292073 \times 10^{-11} \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (3.292073 \times 10^{-11}) = 10.4825 = \mathbf{10.48}$$

- 16.162 The pH is dependent on the *molar* concentration of H₃O⁺. Convert % w/v to concentration (mol/L), and use the *K_a* of acetic acid to determine [H₃O⁺] from the equilibrium expression.
Convert % w/v to concentration (mol/L) using the molecular weight of acetic acid (CH₃COOH):

$$\text{Concentration (mol/L)} = \left(\frac{5.0 \text{ g CH}_3\text{COOH}}{100 \text{ mL solution}} \right) \left(\frac{1 \text{ mol CH}_3\text{COOH}}{60.05 \text{ g CH}_3\text{COOH}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) = 0.832639 \text{ mol/L CH}_3\text{COOH}$$

Acetic acid dissociates in water according to the following equation and equilibrium expression:

	CH ₃ COOH(aq)	+	H ₂ O(l)	⇌	CH ₃ COO ⁻ (aq)	+	H ₃ O ⁺ (aq)
Initial	0.832639		—		0		0
Change	-x				+x		+x
Equilibrium	0.832639 - x				x		x

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639 - x]} \quad \text{Assume } x \text{ is small compared to } 0.832639.$$

$$K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639]}$$

$$x = 3.8714 \times 10^{-3} \text{ mol/L} = [\text{H}^+]$$

Check assumption: $[3.871 \times 10^{-3} / 0.832639] \times 100\% = 0.46\%$, therefore the assumption is good.

$$\text{pH} = -\log [\text{H}^+] = -\log (3.8714 \times 10^{-3}) = 2.412132 = \mathbf{2.41}$$

- 16.164 Plan: Assuming that the pH in the specific cellular environment is equal to the optimum pH for the enzyme, the hydronium ion concentrations are $[H^+] = 10^{-pH}$.

Solution:

Salivary amylase, mouth: $[H^+] = 10^{-6.8} = 1.58489 \times 10^{-7} = \mathbf{2 \times 10^{-7} \text{ mol/L}}$

Pepsin, stomach: $[H^+] = 10^{-2.0} = \mathbf{1 \times 10^{-2} \text{ mol/L}}$

Trypsin, pancreas: $[H^+] = 10^{-9.5} = 3.1623 \times 10^{-10} = \mathbf{3 \times 10^{-10} \text{ mol/L}}$

- 16.168 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 $i = 1$.

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

This molality is the total molality of all species in the solution, and is equal to their concentration (mol/L).

From the equilibrium:

	$\text{ClCH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClCH}_2\text{COO}^-(aq)$		
Initial	1.000 mol/L	x	x
Change	-x	+x	+x
Equilibrium	1.000 - x	x	x

The total concentration of all species is:

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

$$[1.000 - x] + [x] + [x] = 1.000 + x = 1.037634 \text{ mol/L}$$

$$x = 0.037634 \text{ mol/L}$$

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

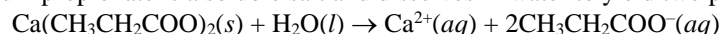
$$K_a = \frac{(0.037634)(0.037634)}{(1.000 - 0.037634)} = 0.0014717 = \mathbf{0.00147}$$

- 16.170 a) The two ions that comprise this salt are 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.

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



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



The concentration (mol/L) of the solution is:

Concentration (mol/L) =

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

$$= 0.1879497 \text{ mol/L CH}_3\text{CH}_2\text{COO}^-$$

	$\text{CH}_3\text{CH}_2\text{COO}^-$	+	H_2O	\rightleftharpoons	$\text{CH}_3\text{CH}_2\text{COOH}$	+	OH^-
Initial	0.1879497 mol/L				0		0
Change	-x				+x		+x
Equilibrium	0.1879497 - x				x		x

$$K_b = K_w/K_a = (1.0 \times 10^{-14})/(1.3 \times 10^{-5}) = 7.69231 \times 10^{-10}$$

$$K_b = 7.69231 \times 10^{-10} = \frac{[\text{CH}_3\text{CH}_2\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]}$$

$$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.1879497 - x)}$$

Assume x is small compared to 0.1879497.

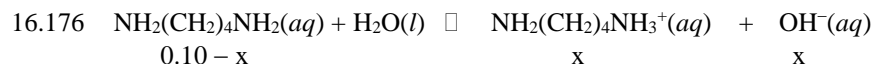
$$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.1879497)}$$

$$x = 1.202401 \times 10^{-5} \text{ mol/L} = [\text{OH}^-]$$

Check assumption: $[1.202401 \times 10^{-5} / 0.1879497] \times 100\% = 0.006\%$, therefore the assumption is good.

$$[\text{H}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.202401 \times 10^{-5}) = 8.31669 \times 10^{-10} \text{ mol/L } \text{H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log (8.31669 \times 10^{-10}) = 9.0800 = \mathbf{9.08}$$



$$x = [\text{OH}^-] = 2.1 \times 10^{-3}$$

$$K_b = \frac{[\text{NH}_2(\text{CH}_2)_4\text{NH}_3^+][\text{OH}^-]}{[\text{NH}_2(\text{CH}_2)_4\text{NH}_2]} = \frac{[2.1 \times 10^{-3}][2.1 \times 10^{-3}]}{[0.10 - 2.1 \times 10^{-3}]} = 4.5045965 \times 10^{-5} = \mathbf{4.5 \times 10^{-5}}$$

16.179 Plan: Use Le Chatelier's principle.

Solution:

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 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 O_2 .

16.181 Plan: The concentration (mol/L) of the acid is calculated by dividing moles of acid by the volume of solution. Set up a reaction table for the dissociation of the acid, in which x = the amount of propanoate ion at equilibrium. The freezing point depression is used to calculate the apparent molality and thus the apparent concentration (mol/L) of the solution. The total concentration of all species at equilibrium equals the apparent concentration (mol/L) and is used to find x . Percent dissociation is the concentration of dissociated acid divided by the initial concentration of the acid and multiplied by 100.

Solution:

a) Calculate the concentration (mol/L) of the solution (before acid dissociation).

$$c = \left(\frac{7.500 \text{ g } \text{CH}_3\text{CH}_2\text{COOH}}{100.0 \text{ mL solution}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol } \text{CH}_3\text{CH}_2\text{COOH}}{74.08 \text{ g } \text{CH}_3\text{CH}_2\text{COOH}} \right) = 1.012419 \text{ mol/L}$$

$$= \mathbf{1.012 \text{ mol/L } \text{CH}_3\text{CH}_2\text{COOH}}$$

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

$$\Delta T = iK_f m = [0.000 - (-1.890^\circ\text{C})] = 1.890^\circ\text{C}$$

Temporarily assume $i = 1$.

$$m = \frac{\Delta T}{iK_f} = \frac{1.890^\circ\text{C}}{(1)(1.86^\circ\text{C/m})} = 1.016129032 \text{ m} = 1.016129032 \text{ mol/L}$$

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

From the equilibrium:

	$\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons$	$\text{H}_3\text{O}^+(aq) +$	$\text{CH}_3\text{CH}_2\text{COO}^-(aq)$
Initial	1.012419 mol/L	0	0
Change	-x	+x	+x
Equilibrium	1.012419 - x	x	x

The total concentration of all species is:

$$[\text{CH}_3\text{CH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{CH}_3\text{CH}_2\text{COO}^-] = 1.016129032 \text{ mol/L}$$

$$[1.012419 - x] + [x] + [x] = 1.012419 + x = 1.016129032 \text{ mol/L}$$

$$x = 0.00371003 = \mathbf{0.004 \text{ mol/L } \text{CH}_3\text{CH}_2\text{COO}^-}$$

c) The percent dissociation is the amount dissociated (x from part b)) divided by the original concentration from part a).

$$\text{Percent dissociation} = \frac{0.00371003 \text{ mol/L}}{1.012419 \text{ mol/L}} (100\%) = 0.366452\% = \mathbf{0.4\%}$$

16.182 Plan: For parts a) and b), write the base-dissociation reaction and the K_b expression. Set up a reaction table in which x = the amount of reacted base and the concentration of OH^- . Solve for x, calculate $[\text{H}_3\text{O}^+]$, and find the pH. For parts c) and d), write the acid-dissociation reaction for the conjugate acid of quinine. Find the K_a value from $K_w = K_a \times K_b$. Set up a reaction table in which x = dissociated acid and the concentration of $[\text{H}_3\text{O}^+]$, and find the pH.

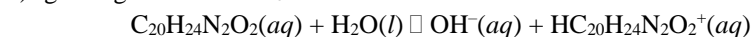
Solution:

Note that both $\text{p}K_b$ values only have one significant figure. This will limit the final answers.

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

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

a) Ignoring the smaller K_b :



$$\begin{array}{ccc} \text{Initial} & 1.6 \times 10^{-3} \text{ mol/L} & 0 & 0 \\ \text{Change} & -x & +x & +x \\ \text{Equilibrium} & 1.6 \times 10^{-3} - x & x & x \end{array}$$

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

$$K_b = 7.94328 \times 10^{-6} = \frac{[x][x]}{[1.6 \times 10^{-3} - x]} \quad \text{Assume } x \text{ is small compared to } 1.6 \times 10^{-3}.$$

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

$$x = 1.127353 \times 10^{-4}$$

Check assumption that x is small compared to 1.6×10^{-3} :

$$\frac{1.127353 \times 10^{-4}}{1.6 \times 10^{-3}} (100\%) = 7\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 1.6×10^{-3} , and it is necessary to use the quadratic equation.

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

$$x^2 + 7.94328 \times 10^{-6}x - 1.270925 \times 10^{-8} = 0$$

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

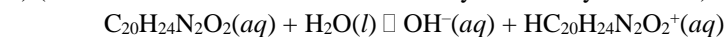
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-7.94328 \times 10^{-6} \pm \sqrt{(7.94328 \times 10^{-6})^2 - 4(1)(-1.270925 \times 10^{-8})}}{2(1)} = 1.08834 \times 10^{-4} \text{ mol/L OH}^-$$

$$[\text{H}]^+ = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.08834 \times 10^{-4}} = 9.18830513 \times 10^{-11} \text{ mol/L H}^+$$

$$\text{pH} = -\log [\text{H}^+] = -\log (9.18830513 \times 10^{-11}) = 10.03676 = \mathbf{10.0}$$

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



$$\begin{array}{ccc} \text{Initial} & 1.6 \times 10^{-3} \text{ mol/L} & 0 & 0 \\ \text{Change} & -x & +x & +x \\ \text{Equilibrium} & 1.6 \times 10^{-3} - x & x & x \end{array}$$

$$\text{Equilibrium } 1.6 \times 10^{-3} - x \quad x \quad x$$

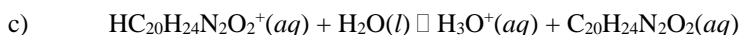
$$K_b = 1.995262 \times 10^{-10} = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}$$

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

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

$$x = 5.65015 \times 10^{-7} \text{ mol/L OH}^-$$

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).



Initial	0.33 mol/L	0	0
Change	-x	+x	+x
Equilibrium	0.33 - x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{7.94328 \times 10^{-6}} = 1.25893 \times 10^{-9}$$

$$K_a = 1.25893 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.33 - x)} \quad \text{Assume } x \text{ is small compared to } 0.33.$$

$$K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.33)}$$

$$[\text{H}^+] = x = 2.038252 \times 10^{-5} \text{ mol/L}$$

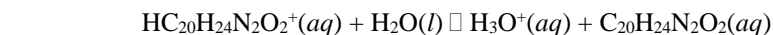
Check assumption that x is small compared to 0.33:

$$\frac{2.038252 \times 10^{-5}}{0.33} (100\%) = 0.006\%. \quad \text{The assumption is good.}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (2.038252 \times 10^{-5}) = 4.69074 = \mathbf{4.7}$$

d) Quinine hydrochloride will be indicated as QHCl.

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



Initial	0.041566 mol/L	0	0
Change	-x	+x	+x
Equilibrium	0.041566 - x	x	x

$$K_a = 1.25893 \times 10^{-9} = \frac{[\text{H}_3\text{O}^+][\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+]}$$

$$K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.041566 - x)} \quad \text{Assume } x \text{ is small compared to } 0.041566.$$

$$K_a = 1.25893 \times 10^{-9} = \frac{(x)(x)}{(0.041566)}$$

$$[\text{H}_3\text{O}^+] = x = 7.233857 \times 10^{-6} \text{ mol/L}$$

Check assumption that x is small compared to 0.33:

$$\frac{7.233857 \times 10^{-6}}{0.041566}(100\%) = 0.02\%. \text{ The assumption is good.}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (7.233857 \times 10^{-6}) = 5.1406 = \mathbf{5.1}$$