

CHAPTER 18 ACID-BASE EQUILIBRIA

FOLLOW-UP PROBLEMS

18.1A **Plan:** Examine the formulas and classify each as an acid or base. Strong acids are the hydrohalic acids HCl, HBr, and HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by at least two. Other acids are weak acids. Strong bases are soluble oxides or hydroxides of the Group 1A(1) metals and Ca, Sr, and Ba in Group 2A(2). Other bases are weak bases.

Solution:

a) Chloric acid, **HClO₃**, is the stronger acid because acid strength increases as the number of O atoms in the acid increases.

b) Hydrochloric acid, **HCl**, is one of the strong hydrohalic acids whereas acetic acid, CH₃COOH, is a weak carboxylic acid.

c) Sodium hydroxide, **NaOH**, is a strong base because Na is a Group 1A(1) metal. Methylamine, CH₃NH₂, is an organic amine and, therefore, a weak base.

18.1B **Plan:** Examine the formulas and classify each as a strong acid, weak acid, strong base, or weak base. Strong acids are the hydrohalic acids HCl, HBr, and HI, and oxoacids in which the number of O atoms exceeds the number of ionizable protons by at least two. Other acids are weak acids. Strong bases are soluble oxides or hydroxides of the Group 1A(1) metals and Ca, Sr, and Ba in Group 2A(2). Other bases are weak bases.

Solution:

a) (CH₃)₃N is a **weak base**. It contains a nitrogen atom with a lone pair of electrons, which classifies it as a base; however, it is not one of the strong bases.

b) Hydroiodic acid, HI, is a **strong acid** (one of the strong acids listed above).

c) HBrO is a **weak acid**. It has an ionizable hydrogen, which makes it an acid. Specifically, it is an oxoacid, in which a polyatomic ion is the anion. In the case of this oxoacid, there is only one O atom for each ionizable hydrogen, so this is a weak acid. The reaction for the dissociation of this weak acid is:

HBrO(aq) + H₂O(l) ⇌ BrO⁻(aq) + H₃O⁺(aq). The corresponding equilibrium expression is:

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

d) Ca(OH)₂ is a **strong base** (one of the strong bases listed above).

18.2A **Plan:** The product of [H₃O⁺] and [OH⁻] remains constant at 25°C because the value of *K_w* is constant at a given temperature. Use *K_w* = [H₃O⁺][OH⁻] = 1.0 × 10⁻¹⁴ to solve for [H₃O⁺].

Solution:

Calculating [H₃O⁺]:

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.7 \times 10^{-2}} = 1.4925 \times 10^{-13} = \mathbf{1.5 \times 10^{-13} M}$$

Since [OH⁻] > [H₃O⁺], the solution is **basic**.

18.2B **Plan:** The product of [H₃O⁺] and [OH⁻] remains constant at 25°C because the value of *K_w* is constant at a given temperature. Use *K_w* = [H₃O⁺][OH⁻] = 1.0 × 10⁻¹⁴ to solve for [H₃O⁺].

Solution:

Calculating [OH⁻]:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-10}} = 5.55555 \times 10^{-5} = \mathbf{5.6 \times 10^{-5} M}$$

Since [OH⁻] > [H₃O⁺], the solution is **basic**.

18.3A **Plan:** NaOH is a strong base that dissociates completely in water. Subtract pH from 14.00 to find the pOH, and calculate inverse logs of pH and pOH to find [H₃O⁺] and [OH⁻], respectively.

Solution:

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pOH} = 14.00 - 9.52 = \mathbf{4.48}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.52} = 3.01995 \times 10^{-10} = \mathbf{3.0 \times 10^{-10} M}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.48} = 3.3113 \times 10^{-5} = \mathbf{3.3 \times 10^{-5} M}$$

- 18.3B Plan: HCl is a strong acid that dissociates completely in water. Subtract pH from 14.00 to find the pOH, and calculate inverse logs of pH and pOH to find $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$, respectively.

Solution:

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pOH} = 14.00 - 2.28 = \mathbf{11.72}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.28} = 5.2481 \times 10^{-3} = \mathbf{5.2 \times 10^{-3} M}$$

$$\text{pOH} = -\log [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.72} = 1.9055 \times 10^{-12} = \mathbf{1.9 \times 10^{-12} M}$$

- 18.4A Plan: Identify the conjugate pairs by first identifying the species that donates H^+ (the acid) in either reaction direction. The other reactant accepts the H^+ and is the base. The acid has one more H and +1 greater charge than its conjugate base.

Solution:

a) CH_3COOH has one more H^+ than CH_3COO^- . H_3O^+ has one more H^+ than H_2O . Therefore, CH_3COOH and H_3O^+ are the acids, and CH_3COO^- and H_2O are the bases. The conjugate acid/base pairs are

$\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$.

b) H_2O donates a H^+ and acts as the acid. F^- accepts the H^+ and acts as the base. In the reverse direction, HF acts as the acid and OH^- acts as the base. The conjugate acid/base pairs are **$\text{H}_2\text{O}/\text{OH}^-$ and HF/F^- .**

- 18.4B Plan: To derive the formula of a conjugate base, remove one H from the acid and decrease the charge by 1 (acids donate H^+). To derive the formula of a conjugate acid, add an H and increase the charge by 1 (bases accept H^+).

Solution:

a) Adding a H^+ to HSO_3^- gives the formula of the conjugate acid: **H_2SO_3 .**

b) Removing a H^+ from $\text{C}_5\text{H}_5\text{NH}^+$ gives the formula of the conjugate base: **$\text{C}_5\text{H}_5\text{N}$.**

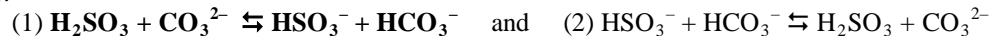
c) Adding a H^+ to CO_3^{2-} gives the formula of the conjugate acid: **HCO_3^- .**

d) Removing a H^+ from HCN gives the formula of the conjugate base: **CN^- .**

- 18.5A 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 ($K_c > 1$) is the one in which the stronger acid produces the weaker acid. The reaction that favors reactants ($K_c < 1$) is the reaction in which the weaker acid produces the stronger acid.

Solution:

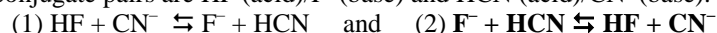
a) The conjugate pairs are H_2SO_3 (acid)/ HSO_3^- (base) and HCO_3^- (acid)/ CO_3^{2-} (base). Two reactions are possible:



The first reaction is the reverse of the second. Both acids are weak. Of the two, H_2SO_3 is the stronger acid.

Reaction (1) with the stronger acid producing the weaker acid favors products and $K_c > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K_c < 1$. Therefore, reaction 1 is the reaction in which $K_c > 1$.

b) The conjugate pairs are HF (acid)/ F^- (base) and HCN (acid)/ CN^- (base). Two reactions are possible:

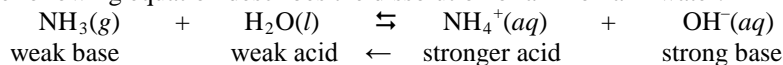


The first reaction is the reverse of the second. Both acids are weak. Of the two, HF is the stronger acid. Reaction (1) with the stronger acid producing the weaker acid favors products and $K_c > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K_c < 1$. Therefore, reaction 2 is the reaction in which $K_c < 1$.

- 18.5B Plan: For a), write the reaction that shows the reaction of ammonia with water; for b), write a reaction between ammonia and HCl; for c), write the reaction between the ammonium ion and NaOH to produce ammonia.

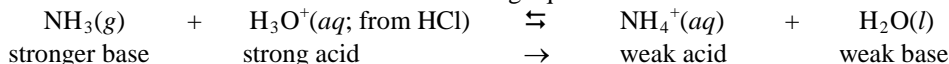
Solution:

a) The following equation describes the dissolution of ammonia in water:



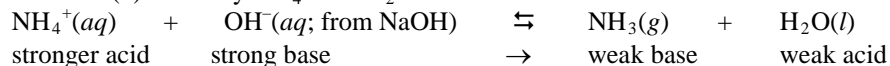
Ammonia is a known weak base, so it makes sense that it accepts a H^+ from H_2O . The reaction arrow indicates that the equilibrium lies to the left because the question states, "you smell ammonia" (NH_3 and OH^- are odorless). NH_4^+ and OH^- are the stronger acid and base, so the reaction proceeds to the formation of the weaker acid and base.

b) The addition of excess HCl results in the following equation:



HCl is a strong acid and is much stronger than NH_4^+ . Similarly, NH_3 is a stronger base than H_2O . The reaction proceeds to produce the weak acid and base, and thus the odor from NH_3 disappears.

c) The solution in (b) is mostly NH_4^+ and H_2O . The addition of excess NaOH results in the following equation:



NH_4^+ and OH^- are the stronger acid and base, respectively, and drive the reaction towards the formation of the weaker base and acid, $\text{NH}_3(g)$ and H_2O , respectively. The reaction direction explains the return of the ammonia odor.

- 18.6A Plan: If HA is a stronger acid than HB, $K_c > 1$ and more HA molecules will produce HB molecules. If HB is a stronger acid than HA, $K_c < 1$ and more HB molecules will produce HA molecules.

Solution:

There are more HB molecules than there are HA molecules, so the equilibrium lies to the right and $K_c > 1$. HA is the stronger acid.

- 18.6B Plan: Because HD is a stronger acid than HC, the reaction of HD and C^- will have $K_c > 1$, and there should be more HC molecules than HD molecules at equilibrium.

Solution:

There are more green/white acid molecules in the solution than black/white acid molecules. Therefore, the green/white acid molecules represent HC, and the black/white acid molecules represent HD. **The green spheres represent C^- , and the black spheres represent D^- .** Because the reaction of the stronger acid HD with C^- will have $K_c > 1$, the reverse reaction ($\text{HC} + \text{D}^-$) will have $K_c < 1$.

- 18.7A Plan: Write a balanced equation for the dissociation of NH_4^+ in water. Using the given information, construct a reaction table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and make assumptions where possible to simplify the calculations. Since the pH is known, $[\text{H}_3\text{O}^+]$ can be found; that value can be substituted into the equilibrium expression.

Solution:

	$\text{NH}_4^+(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{NH}_3(g)$
Initial	0.2 M		_____		0		0
Change	-x		_____		+x		+x
Equilibrium	0.2 - x		_____		x		x

The initial concentration of $\text{NH}_4^+ = 0.2 \text{ M}$ because each mole of NH_4Cl completely dissociates to form one mole of NH_4^+ .

$$x = [\text{H}_3\text{O}^+] = [\text{NH}_3] = 10^{-\text{pH}} = 10^{-5.0} = 1.0 \times 10^{-5} \text{ M}$$

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{(0.2 - x)} = \frac{(1.0 \times 10^{-5})(1.0 \times 10^{-5})}{(0.2 - 1.0 \times 10^{-5})} = 5 \times 10^{-10}$$

- 18.7B Plan: Write a balanced equation for the dissociation of acrylic acid in water. Using the given information, construct a reaction table that describes the initial and equilibrium concentrations. Construct an equilibrium

expression. Since the pH is known, $[\text{H}_3\text{O}^+]$ can be found; that value can be used to find the equilibrium concentrations of all substances, which can then be substituted into the equilibrium expression to solve for the value of K_a .

Solution:

	$\text{H}_2\text{C}=\text{CHCOOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{H}_2\text{C}=\text{CHCOO}^-(aq)$
Initial	0.3 M		_____		0		0
Change	$-x$		_____		$+x$		$+x$
Equilibrium	$0.3 - x$		_____		x		x

According to the information given in the problem, pH at equilibrium = 2.43.

$$[\text{H}_3\text{O}^+]_{\text{eq}} = 10^{-\text{pH}} = 10^{-2.43} = 3.7154 \times 10^{-3} = 3.7 \times 10^{-3} \text{ M} = x$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = [\text{H}_2\text{C}=\text{CHCOO}^-] = 3.7 \times 10^{-3} \text{ M}$$

$$[\text{H}_2\text{C}=\text{CHCOOH}] = (0.30 - x) = (0.30 - 3.7 \times 10^{-3}) \text{ M} = 0.2963 \text{ M}$$

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

$$K_a = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{(0.2963)} = 4.6203 \times 10^{-5} = \mathbf{4.6 \times 10^{-5}}$$

- 18.8A Plan: Write a balanced equation for the dissociation of HOCN in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Construct an equilibrium expression and solve the quadratic expression for x, the concentration of H_3O^+ . Use the concentration of the hydronium ion to solve for pH.

Solution:

	$\text{HOCN}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OCN}^-(aq)$
Initial	0.10 M		_____		0		0
Change	$-x$		_____		$+x$		$+x$
Equilibrium	$0.10 - x$		_____		x		x

$$K_a = 3.5 \times 10^{-4} = \frac{[\text{OCN}^-][\text{H}_3\text{O}^+]}{[\text{HOCN}]} = \frac{x^2}{(0.10 - x)}$$

In this example, the dissociation of HOCN is not negligible in comparison to the initial concentration.

Therefore, the equilibrium expression is solved using the quadratic formula.

$$x^2 = 3.5 \times 10^{-4} (0.10 - x)$$

$$x^2 = 3.5 \times 10^{-5} - 3.5 \times 10^{-4} x$$

$$x^2 + 3.5 \times 10^{-4} x - 3.5 \times 10^{-5} = 0 \quad (ax^2 + bx + c = 0)$$

$$a = 1 \quad b = 3.5 \times 10^{-4} \quad c = -3.5 \times 10^{-5}$$

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

$$x = \frac{-3.5 \times 10^{-4} \pm \sqrt{(3.5 \times 10^{-4})^2 - 4(1)(-3.5 \times 10^{-5})}}{2(1)}$$

$$x = 5.7436675 \times 10^{-3} = \mathbf{5.7 \times 10^{-3} \text{ M H}_3\text{O}^+}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [5.7436675 \times 10^{-3}] = 2.2408 = \mathbf{2.24}$$

- 18.8B Plan: Write a balanced equation for the dissociation of $\text{C}_6\text{H}_5\text{COOH}$ in water. Using the given information, construct a table that describes the initial and equilibrium concentrations. Use $\text{p}K_a$ to solve for the value of K_a . Construct an equilibrium expression, use simplifying assumptions when possible to solve for x, the concentration of H_3O^+ . Use the concentration of the hydronium ion to solve for pH.

Solution:

	$\text{C}_6\text{H}_5\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{C}_6\text{H}_5\text{COO}^-(aq)$
Initial	0.25 M		_____		0		0
Change	$-x$		_____		$+x$		$+x$
Equilibrium	$0.25 - x$		_____		x		x

$$K_a = 10^{-pK_a} = 10^{-4.20} = 6.3096 \times 10^{-5} = 6.3 \times 10^{-5}$$

$$K_a = 6.3 \times 10^{-5} = \frac{[\text{C}_6\text{H}_5\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{(x)(x)}{(0.25 - x)} \quad \text{Assume } x \text{ is negligible so } 0.25 - x \approx 0.25$$

$$\frac{(x)(x)}{(0.25)} = 6.3 \times 10^{-5}$$

$$x^2 = (6.3 \times 10^{-5})(0.25); x = 3.9686 \times 10^{-3} = 4.0 \times 10^{-3}$$

Check the assumption by calculating the % error:

$$\frac{4.0 \times 10^{-3}}{0.25} (100) = 1.6\% \text{ which is smaller than } 5\%, \text{ so the assumption is valid.}$$

At equilibrium $[\text{H}_3\text{O}^+]_{\text{eq}} = 4.0 \times 10^{-3} \text{ M}$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [4.0 \times 10^{-3}] = 2.3979 = 2.40$$

- 18.9A **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 cyanide ion at equilibrium. Then use the initial concentration of HCN and the equilibrium concentration of CN^- to find % dissociation.

Solution:

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

$$K_a = 6.2 \times 10^{-10} = \frac{[\text{CN}^-][\text{H}_3\text{O}^+]}{[\text{HCN}]}$$

$$K_a = 6.2 \times 10^{-10} = \frac{[x][x]}{[0.75 - x]} \quad \text{Assume } x \text{ is small compared to } 0.75.$$

$$K_a = 6.2 \times 10^{-10} = \frac{[x][x]}{[0.75]}$$

$$x = 2.1564 \times 10^{-5} = 2.2 \times 10^{-5} \text{ M}$$

Check the assumption by calculating the % error:

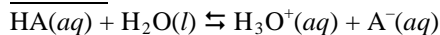
$$\frac{2.2 \times 10^{-5}}{0.75} (100) = 0.0029\% \text{ which is smaller than } 5\%, \text{ so the assumption is valid.}$$

$$\text{Percent HCN dissociated} = \frac{[\text{HCN}]_{\text{dissoc}}}{[\text{HCN}]_{\text{init}}} (100)$$

$$\text{Percent HCN dissociated} = \frac{(2.2 \times 10^{-5})}{0.75} (100) = 0.0029\%$$

- 18.9B **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 $[\text{H}_3\text{O}^+]$. Substitute $[\text{HA}]$, $[\text{A}^-]$, and $[\text{H}_3\text{O}^+]$ into the expression for K_a to find the value of K_a .

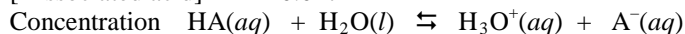
Solution:



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

$$3.16\% = \frac{x}{1.5 \text{ M}} (100)$$

$$[\text{Dissociated acid}] = x = 0.047 \text{ M}$$



Initial:	1.5	0	0
Change:	-x	+x	+x
Equilibrium:	1.5 - x	x	x

[Dissociated acid] = x = [A⁻] = [H₃O⁺] = 0.047 M

[HA] = 1.5 M - 0.047 M = 1.453 M

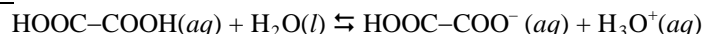
Solving for K_a.

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

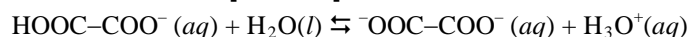
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.047)(0.047)}{(1.453)} = 1.5203 \times 10^{-3} = \mathbf{1.5 \times 10^{-3}}$$

- 18.10A Plan: Write the balanced equation and corresponding equilibrium expression for each dissociation reaction. Calculate the equilibrium concentrations of all species and convert [H₃O⁺] to pH. Find the equilibrium constant values from Appendix C, K_{a1} = 5.6x10⁻² and K_{a2} = 5.4x10⁻⁵.

Solution:



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



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

Assumptions:

- 1) Since K_{a1} >> K_{a2}, the first dissociation produces almost all of the H₃O⁺, so [H₃O⁺]_{eq} = [H₃O⁺] from C₂H₂O₄.
- 2) Since K_{a1} (5.6x10⁻²) is fairly large, solve the first equilibrium expression using the quadratic equation.

	HOOC-COOH(aq)	+ H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+ HOOC-COO ⁻ (aq)
Initial	0.150 M			0	0
Change	-x			+x	+x
Equilibrium	0.150 - x			x	x

$$K_{a1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} = \frac{x^2}{(0.150 - x)} = 5.6 \times 10^{-2}$$

$$x^2 + 5.6 \times 10^{-2}x - 8.4 \times 10^{-3} = 0 \quad (ax^2 + bx + c = 0)$$

$$x = \frac{-5.6 \times 10^{-2} \pm \sqrt{(5.6 \times 10^{-2})^2 - 4(1)(-8.4 \times 10^{-3})}}{2(1)}$$

$$x = 0.067833 \text{ M H}_3\text{O}^+$$

Therefore, [H₃O⁺] = [HC₂O₄⁻] = **0.068 M** and pH = -log(0.067833) = 1.16856 = **1.17**. The oxalic acid concentration at equilibrium is [H₂C₂O₄]_{init} - [H₂C₂O₄]_{dissoc} = 0.150 - 0.067833 = 0.82167 = **0.082 M**.

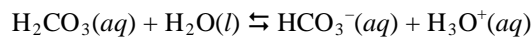
Solve for [C₂O₄²⁻] by rearranging the K_{a2} expression:

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

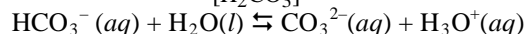
$$[\text{C}_2\text{O}_4^{2-}] = \frac{K_{a2}[\text{HC}_2\text{O}_4^-]}{[\text{H}_3\text{O}^+]} = \frac{(5.4 \times 10^{-5})(0.067833)}{(0.067833)} = \mathbf{5.4 \times 10^{-5} \text{ M}}$$

- 18.10B Plan: Write the balanced equation and corresponding equilibrium expression for each dissociation reaction. Calculate the equilibrium concentrations of all species and convert [H₃O⁺] to pH. Find the equilibrium constant values from Appendix C, K_{a1} = 4.5x10⁻⁷ and K_{a2} = 4.7x10⁻¹¹.

Solution:



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7}$$



$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

Assumption:

1) Since $K_{a1} \gg K_{a2}$, the first dissociation produces almost all of the H_3O^+ , so $[\text{H}_3\text{O}^+]_{\text{eq}} = [\text{H}_3\text{O}^+]$ from H_2CO_3 .

2) Because K_{a1} (4.7×10^{-7}) is fairly small, $[\text{H}_2\text{CO}_3]_{\text{init}} - x \approx [\text{H}_2\text{CO}_3]_{\text{init}}$. Thus,

$$[\text{H}_2\text{CO}_3] = 0.075 \text{ M} - x \approx 0.075 \text{ M}$$

Solve the first equilibrium expression making the assumption that x is small.

	$\text{H}_2\text{CO}_3(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{HCO}_3^-(aq)$
Initial	0.075 M		—————		0		0
Change	-x		—————		+x		+x
Equilibrium	0.075 - x		—————		x		x

$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(x)(x)}{(0.075 - x)} \approx \frac{(x)(x)}{(0.075)} = 4.5 \times 10^{-7}$$

$$x^2 = (0.075)(4.5 \times 10^{-7}); x = 1.8371 \times 10^{-4} = 1.8 \times 10^{-4} \text{ M}$$

Check the assumption by calculating the % error:

$$\frac{1.8 \times 10^{-4}}{0.075} (100) = 0.24\% \text{ which is smaller than } 5\%, \text{ so the assumption is valid.}$$

Therefore, $[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] = 1.8 \times 10^{-4} \text{ M}$ and $\text{pH} = -\log(1.8 \times 10^{-4}) = 3.7447 = 3.74$. The carbonic acid concentration at equilibrium is $[\text{H}_2\text{CO}_3]_{\text{init}} - [\text{H}_2\text{CO}_3]_{\text{dissoc}} = 0.075 - 1.8 \times 10^{-4} = 0.07482 = 0.075 \text{ M} = [\text{H}_2\text{CO}_3]$.

Solve for $[\text{CO}_3^{2-}]$ by rearranging the K_{a2} expression:

$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11}$$

$$[\text{CO}_3^{2-}] = \frac{K_{a2}[\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} = \frac{(4.7 \times 10^{-11})(1.8 \times 10^{-4})}{(1.8 \times 10^{-4})} = 4.7 \times 10^{-11} \text{ M}$$

18.11A Plan: Pyridine contains a nitrogen atom that accepts H^+ from water to form OH^- ions in aqueous solution. Write a balanced equation and equilibrium expression for the reaction, convert $\text{p}K_b$ to K_b , make simplifying assumptions (if valid), and solve for $[\text{OH}^-]$. Calculate $[\text{H}_3\text{O}^+]$ using $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and convert to pH.

Solution:

$$K_b = 10^{-\text{p}K_b} = 10^{-8.77} = 1.69824 \times 10^{-9}$$

	$\text{C}_5\text{H}_5\text{N}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{C}_5\text{H}_5\text{NH}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	0.10 M		—————		0		0
Change	-x		—————		+x		+x
Equilibrium	0.10 - x		—————		x		x

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = 1.69824 \times 10^{-9}$$

Assume that $0.10 - x \approx 0.10$.

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]} = \frac{x^2}{(0.10)} = 1.69824 \times 10^{-9}$$

$$x = 1.303165 \times 10^{-5} = 1.3 \times 10^{-5} \text{ M} = [\text{OH}^-] = [\text{C}_5\text{H}_5\text{NH}^+]$$

Since $\frac{[\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}_5]} (100) = \frac{1.303265 \times 10^{-5}}{0.10} (100) = 0.01313$ which $< 5\%$, the assumption that the dissociation of

$\text{C}_5\text{H}_5\text{N}_5$ is small is valid.

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.303165 \times 10^{-5}} = 7.67362 \times 10^{-10} \text{ M}$$

pH = $-\log(7.67362 \times 10^{-10}) = 9.1149995 = \mathbf{9.11}$ (Since pyridine is a weak base, a pH > 7 is expected.)

- 18.11B **Plan:** Amphetamine contains a nitrogen atom that accepts H^+ from water to form OH^- ions in aqueous solution. Write a balanced equation and equilibrium expression for the reaction, make simplifying assumptions (if valid), and solve for $[\text{OH}^-]$. Calculate $[\text{H}_3\text{O}^+]$ using $[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$ and convert to pH. In the information below, the symbol B will be used to represent the formula of amphetamine.

Solution:

	$\text{B}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{BH}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	0.075 M		————		0		0
Change	-x		————		+x		+x
Equilibrium	0.075 - x		————		x		x

$$K_b = \frac{[\text{BH}][\text{OH}^-]}{[\text{B}]} = 6.3 \times 10^{-5}$$

Assume that $0.075 - x \approx 0.075$.

$$K_b = \frac{[\text{BH}][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{(0.075)} = 6.3 \times 10^{-5}$$

$$x = 0.0021737 = 2.2 \times 10^{-3} \text{ M} = [\text{OH}^-] = [\text{BH}^+]$$

Check the assumption by calculating the % error:

$$\frac{2.2 \times 10^{-3}}{0.075} (100) = 2.9\% \text{ which is smaller than } 5\%, \text{ so the assumption is valid.}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{2.2 \times 10^{-3}} = 4.5 \times 10^{-12} \text{ M}$$

pH = $-\log(4.5 \times 10^{-12}) = 11.3424 = \mathbf{11.35}$

Since amphetamine is a weak base, a pH > 7 is expected.

- 18.12A **Plan:** The hypochlorite ion, ClO^- , acts as a weak base in water. Write a balanced equation and equilibrium expression for this reaction. The K_b of ClO^- is calculated from the K_a of its conjugate acid, hypochlorous acid, HClO (from Appendix C, $K_a = 2.9 \times 10^{-8}$). Make simplifying assumptions (if valid), solve for $[\text{OH}^-]$, convert to $[\text{H}_3\text{O}^+]$ and calculate pH.

Solution:

	$\text{ClO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HClO}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.20 M		————		0		0
Change	-x		————		+x		+x
Equilibrium	0.20 - x		————		x		x

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.448276 \times 10^{-7}$$

Since K_b is very small, assume $[\text{ClO}^-]_{\text{eq}} = 0.20 - x \approx 0.2$.

$$K_b = \frac{[\text{HClO}][\text{OH}^-]}{[\text{ClO}^-]} = \frac{x^2}{(0.20)} = 3.448276 \times 10^{-7}$$

$$x = 2.6261 \times 10^{-4}$$

Therefore, $[\text{HClO}] = [\text{OH}^-] = 2.6 \times 10^{-4} \text{ M}$.

Since $\frac{[\text{OH}^-]}{[\text{ClO}^-]}(100) = \frac{2.6261 \times 10^{-4}}{0.20}(100) = 0.1313$ which $< 5\%$, the assumption that the dissociation of ClO^- is small is valid.

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{2.6261 \times 10^{-4}} = 3.8079 \times 10^{-11} \text{ M}$$

$\text{pH} = -\log(3.8079 \times 10^{-11}) = 10.4193 = \mathbf{10.42}$ (Since hypochlorite ion is a weak base, a $\text{pH} > 7$ is expected.)

18.12B **Plan:** The nitrite ion, NO_2^- , acts as a weak base in water. Write a balanced equation and equilibrium expression for this reaction. The K_b of NO_2^- is calculated from the K_a of its conjugate acid, nitrous acid, HNO_2 (from Appendix C, $K_a = 7.1 \times 10^{-4}$). Make simplifying assumptions (if valid), solve for $[\text{OH}^-]$, convert to $[\text{H}_3\text{O}^+]$ and calculate pH.

Solution:

	$\text{NO}_2^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HNO}_2(aq)$	+	$\text{OH}^-(aq)$
Initial	0.80 M				0		0
Change	-x				+x		+x
Equilibrium	0.80 - x				x		x

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4 \times 10^{-11}$$

Since K_b is very small, assume $[\text{NO}_2^-]_{\text{eq}} = 0.80 - x \approx 0.8$.

$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]} = \frac{x^2}{(0.80)} = 1.4 \times 10^{-11}$$

$$x = 3.3 \times 10^{-6} \text{ M}$$

Check the assumption by calculating the % error:

$$\frac{3.3 \times 10^{-6}}{0.80}(100) = 0.00041\% \text{ which is smaller than } 5\%, \text{ so the assumption is valid.}$$

Therefore, $[\text{HNO}_2] = [\text{OH}^-] = 3.3 \times 10^{-6} \text{ M}$.

$$[\text{H}_3\text{O}^+] = \frac{1 \times 10^{-14}}{3.3 \times 10^{-6}} = 3.0 \times 10^{-9} \text{ M}$$

$\text{pH} = -\log(3.0 \times 10^{-9}) = 8.5229 = \mathbf{8.52}$

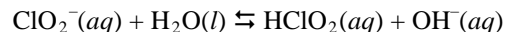
Since nitrite ion is a weak base, a $\text{pH} > 7$ is expected.

18.13A **Plan:** Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

Solution:

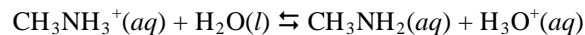
a) The ions are K^+ and ClO_2^- ; the K^+ is from the strong base KOH , and does not react with water. The ClO_2^- is from the weak acid HClO_2 , so it reacts with water to produce OH^- ions. Since the base is strong and the acid is weak, the salt derived from this combination will produce a **basic** solution.

K^+ does not react with water.



b) The ions are CH_3NH_3^+ and NO_3^- ; CH_3NH_3^+ is derived from the weak base methylamine, CH_3NH_2 . Nitrate ion, NO_3^- , is derived from the strong acid HNO_3 (nitric acid). A salt derived from a weak base and strong acid produces an **acidic** solution.

NO_3^- does not react with water.



c) The ions are Rb^+ and Br^- . Rubidium ion is derived from rubidium hydroxide, RbOH , which is a strong base because Rb is a Group 1A(1) metal. Bromide ion is derived from hydrobromic acid, HBr , a strong hydrohalic

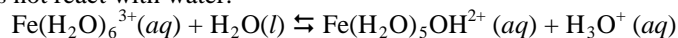
acid. Since both the base and acid are strong, the salt derived from this combination will produce a **neutral** solution.

Neither Rb^+ nor Br^- react with water.

- 18.13B Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

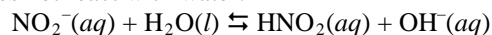
Solution:

a) The ions are Fe^{3+} and Br^- . The Br^- is the anion of the strong acid HBr , so it does not react with water. The Fe^{3+} ion is small and highly charged, so the hydrated ion, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, reacts with water to produce H_3O^+ . Since the base is weak and the acid is strong, the salt derived from this combination will produce an **acidic** solution. Br^- does not react with water.



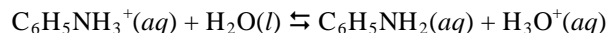
b) The ions are Ca^{2+} and NO_2^- ; the Ca^{2+} is from the strong base $\text{Ca}(\text{OH})_2$, and does not react with water. The NO_2^- is from the weak acid HNO_2 , so it reacts with water to produce OH^- ions. Since the base is strong and the acid is weak, the salt derived from this combination will produce a **basic** solution.

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



c) The ions are $\text{C}_6\text{H}_5\text{NH}_3^+$ and I^- ; $\text{C}_6\text{H}_5\text{NH}_3^+$ is derived from the weak base aniline, $\text{C}_6\text{H}_5\text{NH}_2$. Iodide ion, I^- , is derived from the strong acid HI (hydroiodic acid). A salt derived from a weak base and strong acid produces an **acidic** solution.

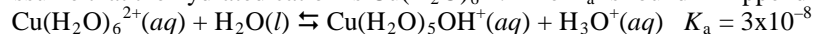
I^- does not react with water.



- 18.14A Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

Solution:

a) The two ions that comprise this salt are cupric ion, Cu^{2+} , and acetate ion, CH_3COO^- . Metal ions are acidic in water. Assume that the hydrated cation is $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. The K_a is found in Appendix C.



Acetate ion acts like a base in water. The K_b is calculated from the K_a of acetic acid (1.8×10^{-5}):

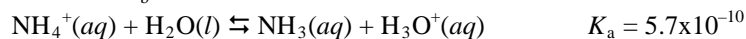
$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$



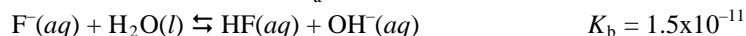
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$ is a better proton donor than CH_3COO^- is a proton acceptor (i.e., $K_a > K_b$), so a solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ is **acidic**.

b) The two ions that comprise this salt are ammonium ion, NH_4^+ , and fluoride ion, F^- . Ammonium ion is the acid

of NH_3 with $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$.

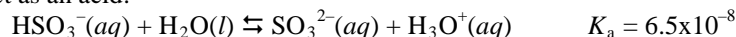


Fluoride ion is the base with $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$.

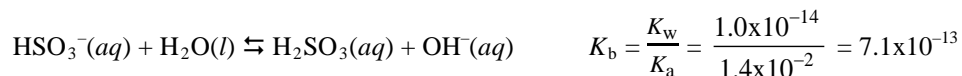


Since $K_a > K_b$, a solution of NH_4F is **acidic**.

c) The ions are K^+ and HSO_3^- ; the K^+ is from the strong base KOH , and does not react with water. The HSO_3^- can react as an acid:



HSO_3^- can also react as a base. Its K_b value can be found by using the K_a of its conjugate acid, H_2SO_3 .



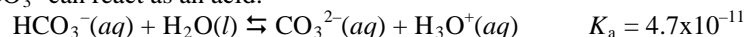
Since $K_a > K_b$, a solution of KHSO_3 is **acidic**.

18.14B Plan: Examine the cations and anions in each compound. If the cation is the cation of a strong base, the cation gives a neutral solution; the cation of a weak base gives an acidic solution. An anion of a strong acid gives a neutral solution while an anion of a weak acid is basic in solution.

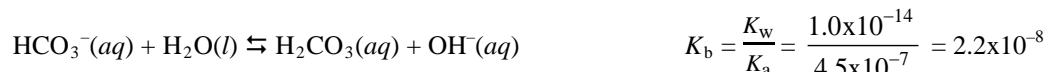
Solution:

a) The two ions that comprise this salt are sodium ion, Na^+ , and bicarbonate ion, HCO_3^- . The Na^+ is from the strong base NaOH , and does not react with water.

The HCO_3^- can react as an acid:



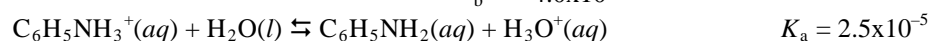
HCO_3^- can also react as a base. Its K_b value can be found by using the K_a of its conjugate acid, H_2CO_3 .



Since $K_b > K_a$, a solution of NaHCO_3 is **basic**.

b) The two ions that comprise this salt are anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$, and nitrite ion, NO_2^- .

Anilinium ion is the acid of $\text{C}_6\text{H}_5\text{NH}_2$ with $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$.

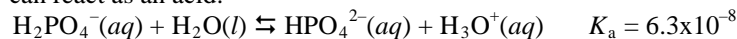


Nitrite ion is the base with $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{7.1 \times 10^{-4}} = 1.4 \times 10^{-11}$.

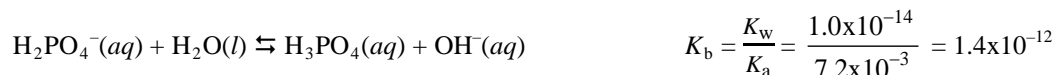


Since $K_a > K_b$, a solution of $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_2$ is **acidic**.

c) The ions are Na^+ and H_2PO_4^- ; the Na^+ is from the strong base NaOH , and does not react with water. The H_2PO_4^- can react as an acid:



H_2PO_4^- can also react as a base. Its K_b value can be found by using the K_a of its conjugate acid, H_3PO_4 .

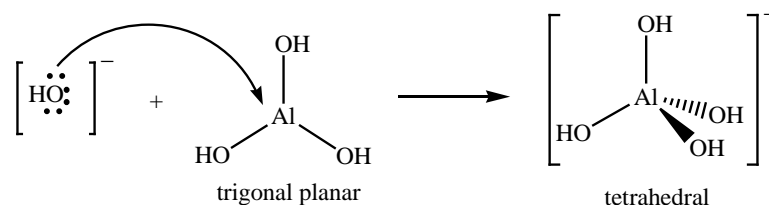


Since $K_a > K_b$, a solution of NaH_2PO_4 is **acidic**.

18.15A Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

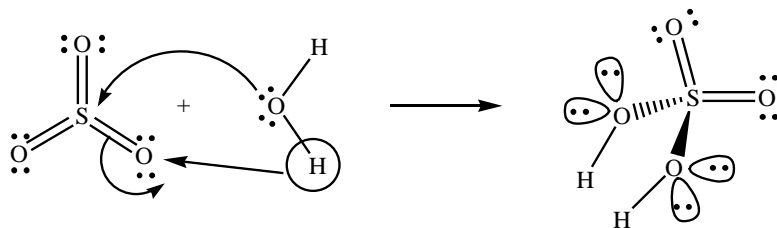
Solution:

a)



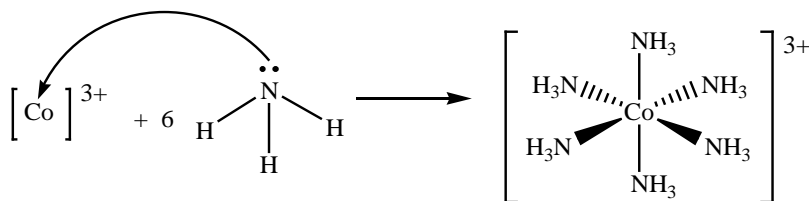
Hydroxide ion, OH^- , donates an electron pair and is the Lewis base; $\text{Al}(\text{OH})_3$ accepts the electron pair and is the Lewis acid. Note the change in geometry caused by the formation of the adduct.

b)



Sulfur trioxide accepts the electron pair and is the Lewis acid. Water donates an electron pair and is the Lewis base.

c)



Co^{3+} accepts six electron pairs and is the Lewis acid. Ammonia donates an electron pair and is the Lewis base.

18.15B Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

Solution:

a) $\text{B}(\text{OH})_3$ is the Lewis acid because it is accepting electron pairs from water, the Lewis base.

b) Cd^{2+} accepts four electron pairs and is the Lewis acid. Each iodide ion donates an electron pair and is the Lewis base.

c) Each fluoride ion donates an electron pair to form a bond with boron in SiF_6^{2-} . The fluoride ion is the Lewis base and the boron tetrafluoride is the Lewis acid.

END-OF-CHAPTER PROBLEMS

- 18.1 The Arrhenius definition classifies substances as being acids or bases by their behavior in the solvent water.
- 18.2 All Arrhenius acids contain hydrogen and produce hydronium ion (H_3O^+) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous solution. Neutralization occurs when each H_3O^+ molecule combines with an OH^- molecule to form two molecules of H_2O . Chemists found that the ΔH_{rxn} was independent of the combination of strong acid with strong base. In other words, the reaction of any strong base with any strong acid always produced 56 kJ/mol ($\Delta H = -56$ kJ/mol). This was consistent with Arrhenius's hypothesis describing neutralization, because all other counter ions (those present from the dissociation of the strong acid and base) were spectators and did not participate in the overall reaction.
- 18.3 The Arrhenius acid-base definition is limited by the fact that it only classifies substances as an acid or base when dissolved in the single solvent water. The anhydrous neutralization of $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ would not be included in the Arrhenius acid-base concept. In addition, it limits a base to a substance that contains OH in its formula. NH_3 does not contain OH in its formula but produces OH^- ions in H_2O .
- 18.4 Strong acids and bases dissociate completely into their ions when dissolved in water. Weak acids only partially dissociate. The characteristic property of all weak acids is that a significant number of the acid molecules are not dissociated. For a strong acid, the concentration of hydronium ions produced by dissolving the acid is equal to the initial concentration of the undissociated acid. For a weak acid, the concentration of hydronium ions produced when the acid dissolves is less than the initial concentration of the acid.
- 18.5 Plan: Recall that an Arrhenius acid contains hydrogen and produces 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**.

18.6 Only (a) **NaHSO₄**

18.7 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.

18.8 (**b**) H_2O is a very weak Arrhenius base.

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

$\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$. The K_a expression is $\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$. $[\text{H}_2\text{O}]$ is treated as a constant

and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

Solution:

a) $\text{HCN}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CN}^-(\text{aq})$

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

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

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

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

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

18.10 a) $\text{CH}_3\text{NH}_3^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{NH}_2(\text{aq})$

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

b) $\text{HClO}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}^-(\text{aq})$

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

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

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

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

$\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$. The K_a expression is $\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$. $[\text{H}_2\text{O}]$ is treated as a constant

and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

Solution:

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

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

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

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

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

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

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

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

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

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

c) $\text{HSO}_4^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{SO}_4^{2-}(aq)$

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

18.13 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:



18.14 **HCl > HNO₂ > HClO > HCN**

18.15 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 1A(1) metal or Ca, Sr, or Ba in Group 2A(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.

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

18.17 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 HNO₃, H₂SO₄, and HClO₄. All other acids are weak acids. Strong bases are metal hydroxides (or oxides) in which the metal is a Group 1A(1) metal or Ca, Sr, or Ba in Group 2A(2). Weak bases are NH₃ and amines.

Solution:

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

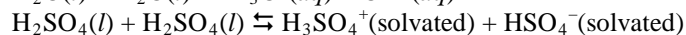
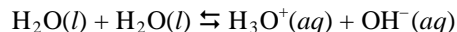
b) Hydrobromic acid, HBr, is a **strong acid**, because it is one of the listed hydrohalic acids.

c) Hydrogen telluride, H₂Te, 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.

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

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



18.20 $\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

[H₂O] is a constant and is included with the value of K_c to obtain K_w:

$$K_w = [\text{H}_2\text{O}]^2 \times K_c = [\text{H}_3\text{O}^+][\text{OH}^-]$$

18.21 a) pH increases by a value of 1.
b) [H₃O⁺] increases by a factor of 1000.

18.22 Plan: The lower the concentration of hydronium (H₃O⁺) ions, the higher the pH. pH increases as K_a or the molarity of acid decreases. Recall that pK_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** = 4x10⁻⁵ has a lower [H₃O⁺] and higher pH.

b) pK_a is equal to -log K_a. The smaller the K_a, the larger the pK_a is. So the **acid with the larger pK_a**, 3.5, has a lower [H₃O⁺] and higher pH.

c) **Lower concentration** of the same acid means lower concentration of hydronium ions produced. The 0.01 M solution has a lower [H₃O⁺] and higher pH.

d) At the same concentration, strong acids dissociate to produce more hydronium ions than weak acids. The 0.1 M solution of a **weak acid** has a lower [H₃O⁺] and higher pH.

e) Bases produce OH⁻ ions in solution, so the concentration of hydronium ion for a solution of a base solution is lower than that for a solution of an acid. The 0.01 M **base solution** has the higher pH.

f) pOH equals -log [OH⁻]. At 25°C, the equilibrium constant for water ionization, K_w, equals 1x10⁻¹⁴ so 14 = pH + pOH. As pOH decreases, pH increases. The solution of **pOH = 6.0** has the higher pH.

18.23 Plan: Part a) can be approached two ways. Because NaOH is a strong base, the [OH⁻]_{eq} = [NaOH]_{init}. One method involves calculating [H₃O⁺] using K_w = [H₃O⁺][OH⁻], then calculating pH from the relationship pH = -log [H₃O⁺]. The other method involves calculating pOH and then using pH + 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:

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

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

- $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.0090 \times 10^{-13}) = 12.04532 = \mathbf{12.05}$
 Second method:
 $\text{pOH} = -\log [\text{OH}^-] = -\log (0.0111) = 1.954677$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.954677 = 12.04532 = \mathbf{12.05}$
 With a $\text{pH} > 7$, the solution is **basic**.
 b) For a strong acid such as HCl:
 $[\text{H}_3\text{O}^+] = [\text{HCl}] = 1.35 \times 10^{-3} \text{ M}$
 $\text{pH} = -\log (1.35 \times 10^{-3}) = 2.869666$
 $\text{pOH} = 14.00 - 2.869666 = 11.130334 = \mathbf{11.13}$
 With a $\text{pH} < 7$, the solution is **acidic**.
- 18.24 a) $\text{pH} = -\log (0.0333) = 1.47756 = \mathbf{1.478}$; **acidic**
 b) $\text{pOH} = -\log (0.0347) = 1.45967 = \mathbf{1.460}$; **basic**
- 18.25 Plan: HI is a strong acid, so $[\text{H}_3\text{O}^+] = [\text{HI}]$ 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) $[\text{H}_3\text{O}^+] = [\text{HI}] = 6.14 \times 10^{-3} \text{ M}$
 $\text{pH} = -\log (6.14 \times 10^{-3}) = 2.211832 = \mathbf{2.212}$. Solution is **acidic**.
 b) $[\text{OH}^-] = 2 \times [\text{Ba}(\text{OH})_2] = 2(2.55 \text{ M}) = 5.10 \text{ M}$
 $\text{pOH} = -\log (5.10) = -0.70757 = \mathbf{-0.708}$. Solution is **basic**.
- 18.26 a) $\text{pOH} = -\log (7.52 \times 10^{-4}) = 3.12378$
 $\text{pH} = 14.00 - 3.12378 = 10.87622 = \mathbf{10.88}$ **basic**
 b) $\text{pH} = -\log (1.59 \times 10^{-3}) = 2.79860$
 $\text{pOH} = 14.00 - 2.79860 = 11.20140 = \mathbf{11.20}$ **acidic**
- 18.27 Plan: The relationships are: $\text{pH} = -\log [\text{H}_3\text{O}^+]$ and $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$; $\text{pOH} = -\log [\text{OH}^-]$ and $[\text{OH}^-] = 10^{-\text{pOH}}$; and $14 = \text{pH} + \text{pOH}$.
Solution:
 a) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.85} = 1.4125375 \times 10^{-10} = \mathbf{1.4 \times 10^{-10} \text{ M H}_3\text{O}^+}$
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 9.85 = \mathbf{4.15}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.15} = 7.0794578 \times 10^{-5} = \mathbf{7.1 \times 10^{-5} \text{ M OH}^-}$
 b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.43 = \mathbf{4.57}$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.57} = 2.691535 \times 10^{-5} = \mathbf{2.7 \times 10^{-5} \text{ M H}_3\text{O}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.43} = 3.7153523 \times 10^{-10} = \mathbf{3.7 \times 10^{-10} \text{ M OH}^-}$
- 18.28 a) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.47} = 3.38844 \times 10^{-4} = \mathbf{3.4 \times 10^{-4} \text{ M H}_3\text{O}^+}$
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 3.47 = \mathbf{10.53}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-10.53} = 2.951209 \times 10^{-11} = \mathbf{3.0 \times 10^{-11} \text{ M OH}^-}$
 b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.33 = \mathbf{9.67}$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.67} = 2.13796 \times 10^{-10} = \mathbf{2.1 \times 10^{-10} \text{ M H}_3\text{O}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.33} = 4.67735 \times 10^{-5} = \mathbf{4.7 \times 10^{-5} \text{ M OH}^-}$
- 18.29 Plan: The relationships are: $\text{pH} = -\log [\text{H}_3\text{O}^+]$ and $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$; $\text{pOH} = -\log [\text{OH}^-]$ and $[\text{OH}^-] = 10^{-\text{pOH}}$; and $14 = \text{pH} + \text{pOH}$.
Solution:
 a) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.77} = 1.69824 \times 10^{-5} = \mathbf{1.7 \times 10^{-5} \text{ M H}_3\text{O}^+}$
 $\text{pOH} = 14.00 - \text{pH} = 14.00 - 4.77 = \mathbf{9.23}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.23} = 5.8884 \times 10^{-10} = \mathbf{5.9 \times 10^{-10} \text{ M OH}^-}$
 b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.65 = \mathbf{8.35}$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.35} = 4.46684 \times 10^{-9} = \mathbf{4.5 \times 10^{-9} \text{ M H}_3\text{O}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.65} = 2.23872 \times 10^{-6} = \mathbf{2.2 \times 10^{-6} \text{ M OH}^-}$
- 18.30 a) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.97} = 1.071519 \times 10^{-9} = \mathbf{1.1 \times 10^{-9} \text{ M H}_3\text{O}^+}$

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 8.97 = \mathbf{5.03}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.03} = 9.3325 \times 10^{-6} = \mathbf{9.3 \times 10^{-6} M \text{ OH}^-}$$

b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 11.27 = \mathbf{2.73}$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.73} = 1.862087 \times 10^{-3} = \mathbf{1.9 \times 10^{-3} M \text{ H}_3\text{O}^+}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.27} = 5.3703 \times 10^{-12} = \mathbf{5.4 \times 10^{-12} M \text{ OH}^-}$$

- 18.31 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 $[\text{H}_3\text{O}^+]$ would be equal to the $[\text{OH}^-]$ added. Use the relationship $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ to find $[\text{H}_3\text{O}^+]$ at each pH.

Solution:

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.15} = 7.07946 \times 10^{-4} M \text{ H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.65} = 2.23872 \times 10^{-4} M \text{ H}_3\text{O}^+$$

$$\text{Add } (7.07946 \times 10^{-4} M - 2.23872 \times 10^{-4} M) = 4.84074 \times 10^{-4} = \mathbf{4.8 \times 10^{-4} \text{ mol of OH}^- \text{ per liter}}$$

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

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.33} = 4.67735 \times 10^{-10} M \text{ H}_3\text{O}^+$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.07} = 8.51138 \times 10^{-10} M \text{ H}_3\text{O}^+$$

$$\text{Add } (8.51138 \times 10^{-10} M - 4.67735 \times 10^{-10} M) = 3.83403 \times 10^{-10} = \mathbf{3.8 \times 10^{-10} \text{ mol of H}_3\text{O}^+ \text{ per liter}}$$

- 18.33 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 $[\text{H}_3\text{O}^+]$ would be equal to the $[\text{OH}^-]$ added. Use the relationship $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$ to find $[\text{H}_3\text{O}^+]$ at each pH.

Solution:

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

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

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

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

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

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

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

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

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

- 18.35 Scene A has a pH of 4.8.

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

Scene B:

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

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

- 18.36 Plan: Apply Le Chatelier's principle in part a). In part b), given that the pH is 6.80, $[\text{H}_3\text{O}^+]$ can be calculated by using the relationship $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$. The problem specifies that the solution is neutral (pure water), meaning $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. 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 .

$$\text{b) } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.80} = 1.58489 \times 10^{-7} M \text{ H}_3\text{O}^+ = \mathbf{1.6 \times 10^{-7} M} \quad [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

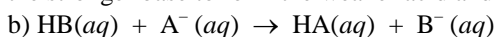
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = \mathbf{2.5 \times 10^{-14}}$$

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

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

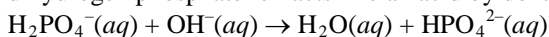
18.38 Every acid has a conjugate base, and every base has a conjugate acid. The acid has one more H and one more positive charge than the base from which it was formed.

18.39 a) Acid-base reactions are proton transfer processes. Thus, the proton will be transferred from the stronger acid to the stronger base to form the weaker acid and weaker base.

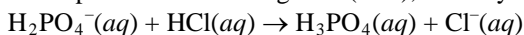


The spontaneous direction of a Brønsted-Lowry acid-base reaction is that the stronger acid will transfer a proton to the stronger base to produce the weaker acid and base. Thus at equilibrium there should be relatively more of weaker acid and base present than there will be of the stronger acid and base. Since there is more HA and B^- in sample and less HB and A^- , HB must be the stronger acid and A^- must be the stronger base.

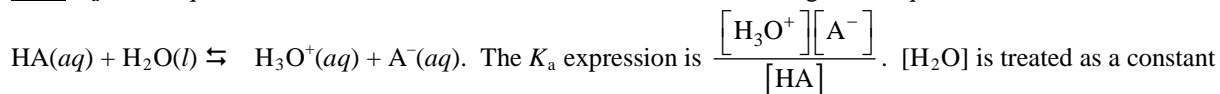
18.40 An amphoteric substance can act as either an acid or a base. In the presence of a strong base (OH^-), the dihydrogen phosphate ion acts like an acid by donating hydrogen:



In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:



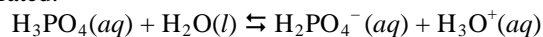
18.41 Plan: K_a is the equilibrium constant for an acid dissociation which has the generic equation



and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

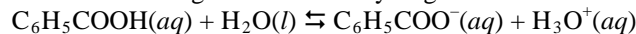
Solution:

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



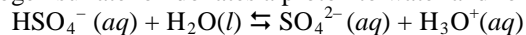
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

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.



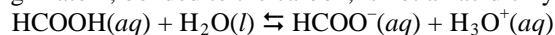
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

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



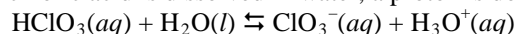
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

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



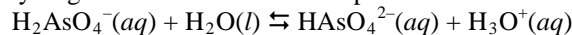
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$$

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



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

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



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

18.43 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^-

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

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

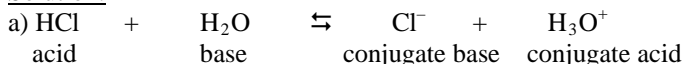
Solution:

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

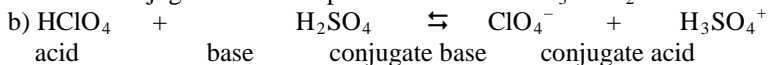
18.46 a) OH^- b) HSO_4^- c) $\text{H}_3\text{O}^{\square+}$

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

Solution:

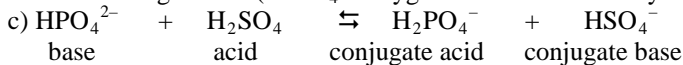


Conjugate acid-base pairs: HCl/Cl^- and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$

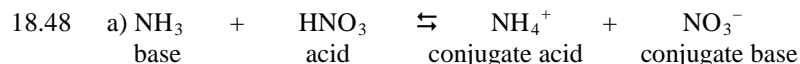


Conjugate acid-base pairs: $\text{HClO}_4/\text{ClO}_4^-$ and $\text{H}_3\text{SO}_4^+/\text{H}_2\text{SO}_4$

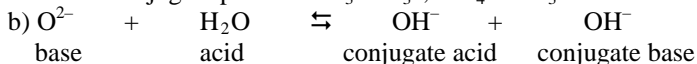
Note: Perchloric acid is able to protonate another strong acid, H_2SO_4 , because perchloric acid is a stronger acid. (HClO_4 's oxygen atoms exceed its hydrogen atoms by one more than H_2SO_4 .)



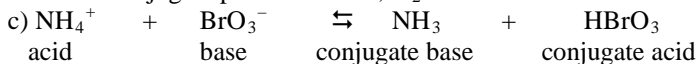
Conjugate acid-base pairs: $\text{H}_2\text{SO}_4/\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$



Conjugate pairs: $\text{HNO}_3/\text{NO}_3^-$; $\text{NH}_4^+/\text{NH}_3$



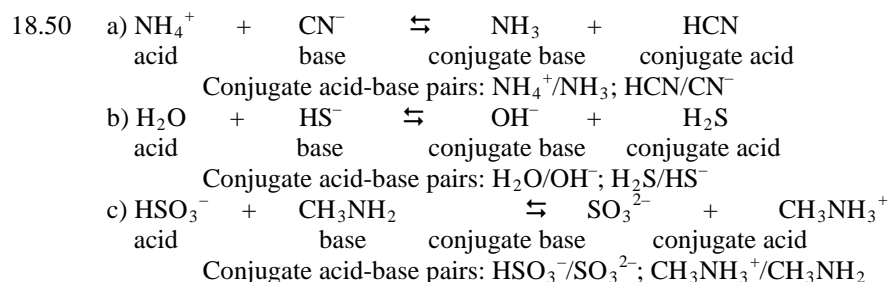
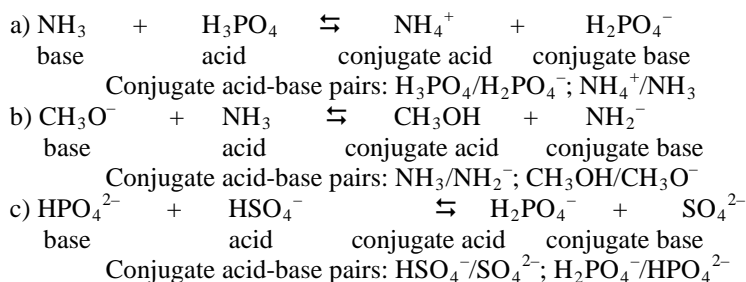
Conjugate pairs: $\text{OH}^-/\text{O}^{2-}$; $\text{H}_2\text{O}/\text{OH}^-$



Conjugate pairs: $\text{NH}_4^+/\text{NH}_3$; $\text{HBrO}_3/\text{BrO}_3^-$

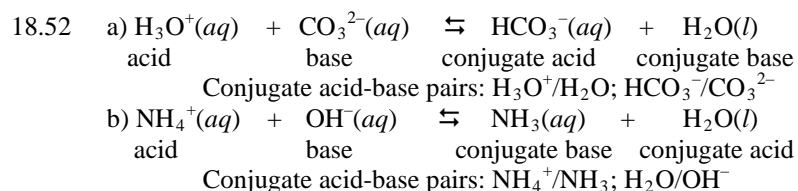
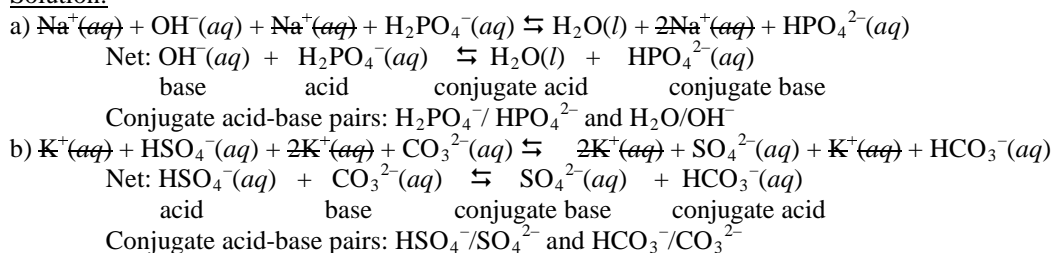
18.49 Plan: The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid.

Solution:



18.51 **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.

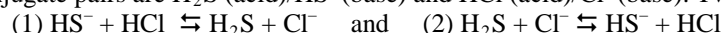
Solution:



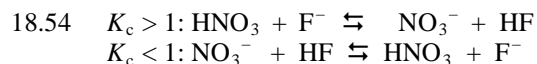
18.53 **Plan:** The two possible reactions involve reacting the acid from one conjugate pair with the base from the other conjugate pair. The reaction that favors the products ($K_c > 1$) is the one in which the stronger acid produces the weaker acid. The reaction that favors reactants ($K_c < 1$) is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

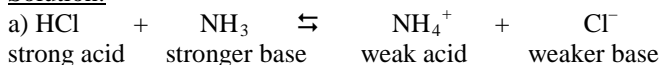


The first reaction is the reverse of the second. HCl is a strong acid and H_2S a weak acid. Reaction (1) with the stronger acid producing the weaker acid favors products and $K_c > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K_c < 1$.

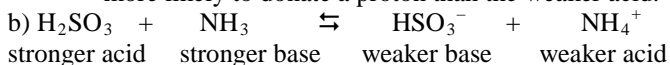


18.55 Plan: An acid-base reaction that favors the products ($K_c > 1$) is one in which the stronger acid produces the weaker acid. Use the figure to decide which of the two acids is the stronger acid.

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 $K_c > 1$. The stronger acid is more likely to donate a proton than the weaker acid.

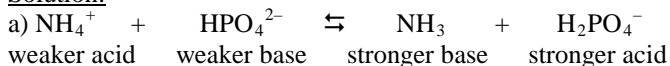


H_2SO_3 is ranked above NH_4^+ and is the stronger acid. NH_3 is a stronger base than HSO_3^- . The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$.

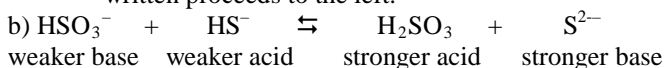
18.56 **Neither a or b have $K_c > 1$.**

18.57 Plan: An acid-base reaction that favors the reactants ($K_c < 1$) 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:



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



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

18.58 a) $K_c < 1$ b) $K_c > 1$

- 18.59 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)

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

18.61 Plan: We are given the percent dissociation of the original HA solution (33%), and we know that the percent dissociation increases as the acid is diluted. Thus, we calculate the percent dissociation of each diluted sample and see which is greater than 33%. To determine percent dissociation, we use the following formula:
Percent HA dissociated = $([\text{HA}]_{\text{dissoc}}/[\text{HA}]_{\text{init}}) \times 100$, with $[\text{HA}]_{\text{dissoc}}$ equal to the number of H_3O^+ (or A^-) ions and $[\text{HA}]_{\text{init}}$ equal to the number of HA *plus* the number of H_3O^+ (or A^-)

Solution:

Calculating the percent dissociation of each diluted solution:

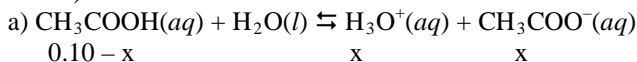
Solution 1. Percent dissociation = $[4/(5+4)] \times 100 = 44\%$

Solution 2. Percent dissociation = $[2/(7+2)] \times 100 = 22\%$

Solution 3. Percent dissociation = $[3/(6+3)] \times 100 = 33\%$

Therefore, scene 1 represents the diluted solution.

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



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

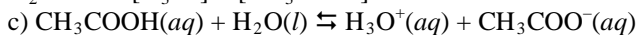
$$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1 - x)} \quad \text{Assume } x \text{ is small compared to } 0.1 \text{ so } 0.1 - x = 0.1.$$

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

$$x = 1.3416 \times 10^{-3} M$$

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

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



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

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

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

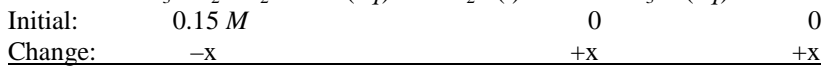
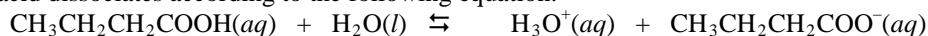
Thus, $[CH_3COO^-] > [H_3O^+]$

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

18.64 Plan: Write the acid-dissociation reaction and the expression for K_a . Set up a reaction table and substitute the given value of $[H_3O^+]$ for x ; solve for K_a .

Solution:

Butanoic acid dissociates according to the following equation:



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

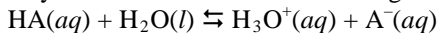
Thus, $[H_3O^+] = [CH_3CH_2CH_2COO^-] = 1.51 \times 10^{-3} M$

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

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

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

18.65 Any weak acid dissociates according to the following equation:



$$[H_3O^+] = 10^{-pH} = 10^{-4.88} = 1.31826 \times 10^{-5} M$$

Thus, $[H_3O^+] = [A^-] = 1.31826 \times 10^{-5} M$, and $[HA] = (0.035 - 1.31826 \times 10^{-5}) = 0.03499 M$

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

$$K_a = \frac{(1.31826 \times 10^{-5})(1.31826 \times 10^{-5})}{(0.03499)} = 4.967 \times 10^{-9} = \mathbf{5.0 \times 10^{-9}}$$

- 18.66 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 ($[\text{H}_3\text{O}^+]$).

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	$\text{HNO}_2(aq)$	+	$\text{H}_2\text{O}(l)$	\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:

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

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

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

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

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

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

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

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

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

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

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

$$x = 0.02258$$

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

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

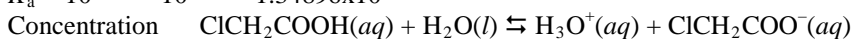
$$[\text{OH}^-] = 1.0 \times 10^{-14} / 0.02258 = 4.42869796 \times 10^{-13} = \mathbf{4.4 \times 10^{-13} M OH^-}$$

- 18.68 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 ($[H_3O^+]$). K_a is found from the pK_a by using the relationship $K_a = 10^{-pK_a}$.

Solution:

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



$$\text{Initial} \quad 1.25 \quad 0 \quad 0$$

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

$$\text{Equilibrium} \quad 1.25 - x \quad x \quad x$$

$$K_a = 1.34896 \times 10^{-3} = \frac{[H_3O^+][ClCH_2COO^-]}{[ClCH_2COOH]}$$

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

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

$$x = 0.04106337$$

Check assumption that x is small compared to 1.25:

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

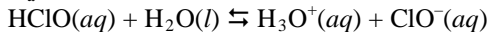
$$[H_3O^+] = [ClCH_2COO^-] = \mathbf{0.041 M}$$

$$[ClCH_2COOH] = 1.25 - 0.04106337 = 1.20894 = \mathbf{1.21 M}$$

$$pH = -\log [H_3O^+] = -\log (0.04106337) = 1.3865 = \mathbf{1.39}$$

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

$$K_a = 10^{-pK_a} = 10^{-7.54} = 2.88403 \times 10^{-8}$$



$$0.115 - x \quad x \quad x$$

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

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

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

$$x = 5.75902 \times 10^{-5}$$

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

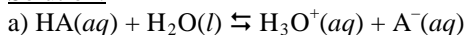
$$[H_3O^+] = [ClO^-] = \mathbf{5.8 \times 10^{-5} M}$$

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

$$pH = -\log [H_3O^+] = -\log (5.75902 \times 10^{-5}) = 4.2397 = \mathbf{4.24}$$

- 18.70 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 $[H_3O^+]$. 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 $[H_3O^+]$. pH and $[OH^-]$ are determined from $[H_3O^+]$. Substitute $[HA]$, $[A^-]$, and $[H_3O^+]$ into the expression for K_a to find the value of K_a .

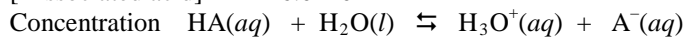
Solution:



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

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

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



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

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

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

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (6.0 \times 10^{-3}) = 2.22185 = \mathbf{2.22}$$

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

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-3}} = 1.6666667 \times 10^{-12} = \mathbf{1.7 \times 10^{-12} M}$$

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

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

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

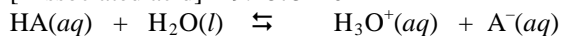
18.71 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of A^- and H_3O^+ . Then, pH and $[\text{OH}^-]$ are determined from $[\text{H}_3\text{O}^+]$.

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

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

$$[\text{Dissociated acid}] = 9.1875 \times 10^{-2} M$$



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

$$[\text{Dissociated acid}] = x = [\text{H}_3\text{O}^+] = \mathbf{9.19 \times 10^{-2} M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.1875 \times 10^{-2}) = 1.03680 = \mathbf{1.037}$$

$$[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(9.1875 \times 10^{-2}) = 1.0884 \times 10^{-13} = \mathbf{1.1 \times 10^{-13} M}$$

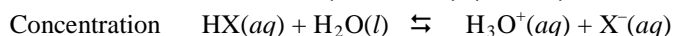
$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.0884 \times 10^{-13}) = 12.963197 = \mathbf{12.963}$$

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{(9.1875 \times 10^{-2})(9.1875 \times 10^{-2})}{(0.735 - 9.1875 \times 10^{-2})} = 1.3125 \times 10^{-2} = \mathbf{1.31 \times 10^{-2}}$$

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

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



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

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

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

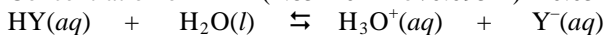
$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.54} = 2.88403 \times 10^{-4} M = x$$

$$\text{Thus, } [\text{H}_3\text{O}^+] = [\text{X}^-] = 2.88403 \times 10^{-4} M, \text{ and } [\text{HX}] = (0.381679 - 2.88403 \times 10^{-4}) M$$

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

- 18.73 Calculate the molarity of HY by dividing moles by volume. Convert pH to $[\text{H}_3\text{O}^+]$ and substitute into the equilibrium expression.

Concentration of HY = $(4.85 \times 10^{-3} \text{ mol} / 0.095 \text{ L}) = 0.0510526 \text{ M}$



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

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-2.68} = 2.089296 \times 10^{-3} \text{ M} = x$$

Thus, $[\text{H}_3\text{O}^+] = [\text{Y}^-] = 2.089296 \times 10^{-3} \text{ M}$, and $[\text{HY}] = (0.0510526 - 2.089296 \times 10^{-3}) \text{ M}$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{(2.089296 \times 10^{-3})(2.089296 \times 10^{-3})}{(0.0510526 - 2.089296 \times 10^{-3})} = 8.91516 \times 10^{-5} = \mathbf{8.9 \times 10^{-5}}$$

- 18.74 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 ($[\text{H}_3\text{O}^+]$). OH^- and then pOH can be found from $[\text{H}_3\text{O}^+]$.

Solution:

a) Concentration	$\text{HZ}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Z}^-(aq)$
Initial	0.075		—		0		0
Change	-x				+x		+x
Equilibrium	$0.075 - x$				x		x

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

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

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

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

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

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.)

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

b) Concentration	$\text{HZ}(aq)$	+	$\text{H}_2\text{O}(l)$	\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_3O^+ contribution from water has been neglected.)

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

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

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

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

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.

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

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

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

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

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

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

$$x = 3.26238 \times 10^{-3} \text{ M } \text{H}_3\text{O}^+$$

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

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

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

$$K_a = 10^{-\text{p}K_a} = 10^{-4.89} = 1.28825 \times 10^{-5}$$

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

Concentration	$\text{HQ}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{Q}^-(aq)$
Initial	0.035		—		0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.035 - x$				x		x

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

$$K_a = 1.28825 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Q}^-]}{[\text{HQ}]}$$

$$K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.035 - x)} \quad \text{Assume } x \text{ is small compared to } 0.035.$$

$$K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.035)}$$

$$[\text{H}_3\text{O}^+] = x = 6.71482 \times 10^{-4} \text{ M}$$

Check assumption: $(6.71482 \times 10^{-4} / 0.035) \times 100\% = 2\%$ error, so the assumption is valid.

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

b) Concentration	HQ(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	Q ⁻ (aq)
Initial	0.65		—		0		0
Change	-x				+x		+x
Equilibrium	0.65 - x				x		x

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

$$K_a = 1.28825 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Q}^-]}{[\text{HQ}]}$$

$$K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.65 - x)} \quad \text{Assume } x \text{ is small compared to } 0.65.$$

$$K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.65)}$$

$$[\text{H}_3\text{O}^+] = x = 2.89372 \times 10^{-3} \text{ M}$$

Check assumption: $(2.89372 \times 10^{-3} / 0.65) \times 100\% = 0.4\%$ error, so the assumption is valid.

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (2.89372 \times 10^{-3}) = 3.4558 \times 10^{-12} = \mathbf{3.5 \times 10^{-12} \text{ M}}$$

- 18.76 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 ($[\text{H}_3\text{O}^+]$). OH^- and then pOH can be found from $[\text{H}_3\text{O}^+]$.

Solution:

a) Concentration	HY(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	Y ⁻ (aq)
Initial	0.175		—		0		0
Change	-x				+x		+x
Equilibrium	0.175 - x				x		x

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

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

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

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

$$[\text{H}_3\text{O}^+] = x = 5.1235 \times 10^{-3} \text{ M}$$

Check assumption that x is small compared to 0.175:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.1235 \times 10^{-3}) = 2.29043 = \mathbf{2.290}$$

b) Concentration	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.)

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

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

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

$$[\text{H}_3\text{O}^+] = x = 5.9161 \times 10^{-2} \text{ M}$$

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.

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

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

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

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

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

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

$$x = 5.00 \times 10^{-2} \text{ M } \text{H}_3\text{O}^+$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{5.00 \times 10^{-2}} = 2.00 \times 10^{-13} \text{ M}$$

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

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

Concentration	$\text{HCN}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{CN}^-(aq)$
Initial	0.55		—		0		0
Change	-x				+x		+x
Equilibrium	$0.55 - x$				x		x

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

$$K_a = 6.2 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 1.84662 \times 10^{-5} \text{ M}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.84662 \times 10^{-5}) = 4.7336 = \mathbf{4.73}$$

b) Begin this part like part a).

Concentration	$\text{HIO}_3(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{IO}_3^-(aq)$
Initial	0.044		—		0		0
Change	-x				+x		+x
Equilibrium	$0.044 - x$				x		x

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

$$K_a = 0.16 = \frac{[\text{H}_3\text{O}^+][\text{IO}_3^-]}{[\text{HIO}_3]}$$

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

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

$$[\text{H}_3\text{O}^+] = x = 8.3905 \times 10^{-2}$$

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

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

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

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

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

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

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

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

$$x = 0.03593 \text{ M } \text{H}_3\text{O}^+$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (0.03593) = 2.78 \times 10^{-13} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.78 \times 10^{-13}) = 12.55596 = \mathbf{12.56}$$

- 18.78 **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 benzoate ion at equilibrium. Then use the initial concentration of benzoic acid and the equilibrium concentration of benzoate to find % dissociation.

Solution:

Concentration	$\text{C}_6\text{H}_5\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{C}_6\text{H}_5\text{COO}^-(aq)$
Initial	0.55		—		0		0
Change	-x				+x		+x
Equilibrium	$0.55 - x$				x		x

$$K_a = 6.3 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$$

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

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

$$x = 5.8864 \times 10^{-3} \text{ M}$$

$$\text{Percent } \text{C}_6\text{H}_5\text{COOH} \text{ dissociated} = \frac{[\text{C}_6\text{H}_5\text{COOH}]_{\text{dissociated}}}{[\text{C}_6\text{H}_5\text{COOH}]_{\text{initial}}} (100)$$

$$\text{Percent } \text{C}_6\text{H}_5\text{COOH} \text{ dissociated} = \frac{5.8864 \times 10^{-3} \text{ M}}{0.55 \text{ M}} (100) = 1.07025 = \mathbf{1.1\%}$$

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

Concentration	$\text{CH}_3\text{COOH}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{CH}_3\text{COO}^-(aq)$
Initial	0.050		—		0		0
<u>Change</u>	-x				+x		+x
Equilibrium	$0.050 - x$				x		x

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

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

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

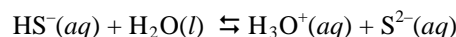
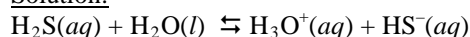
$$x = 9.48683 \times 10^{-4} \text{ M}$$

$$\text{Percent } \text{CH}_3\text{COOH} \text{ dissociated} = \frac{[\text{CH}_3\text{COOH}]_{\text{dissociated}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} (100)$$

$$\text{Percent } \text{CH}_3\text{COOH} \text{ dissociated} = \frac{9.48683 \times 10^{-4}}{0.050} (100) = 1.897367 = \mathbf{1.9\%}$$

- 18.80 Plan: Write balanced chemical equations and corresponding equilibrium expressions for dissociation of hydrosulfuric acid, H_2S , and HS^- . Since $K_{a1} \gg K_{a2}$, 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 $[\text{H}_3\text{O}^+]$.

Solution:



$$K_{a1} = 9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

$$K_{a2} = 1 \times 10^{-17} = \frac{[\text{H}_3\text{O}^+][\text{S}^{2-}]}{[\text{HS}^-]}$$

Concentration	$\text{H}_2\text{S}(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{HS}^-(aq)$
Initial	0.10		—		0		0
<u>Change</u>	-x				+x		+x
Equilibrium	$0.10 - x$				x		x

$$K_{a1} = 9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

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

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

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

$$[\text{H}_3\text{O}^+] = [\text{HS}^-] = x = \mathbf{9 \times 10^{-5} \text{ M}}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.48683 \times 10^{-5}) = 4.022878 = \mathbf{4.0}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{9.48683 \times 10^{-5}} = 1.05409 \times 10^{-10} = \mathbf{1 \times 10^{-10} \text{ M}}$$

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

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

Concentration is limited to one significant figure because K_a is given to only one significant figure. The pH is given to what appears to be 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 $[S^{2-}]$ by using the K_{a2} expression and assuming that $[HS^-]$ and $[H_3O^+]$ come mostly from the first dissociation. This new calculation will have a new x value.

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

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

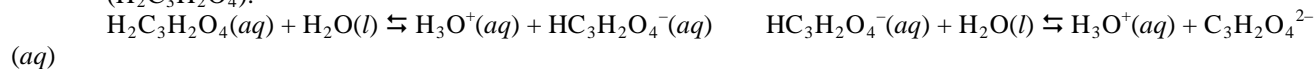
$$K_{a2} = 1 \times 10^{-17} = \frac{(9.48683 \times 10^{-5} + x)(x)}{(9.48683 \times 10^{-5} - x)} \quad \text{Assume } x \text{ is small compared to } 9.48683 \times 10^{-5}.$$

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

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

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

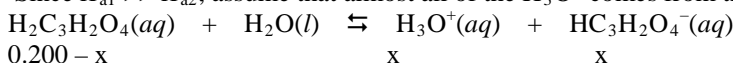
18.81 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of malonic acid ($H_2C_3H_2O_4$).



$$K_{a1} = 1.4 \times 10^{-3} = \frac{[H_3O^+][HC_3H_2O_4^-]}{[H_2C_3H_2O_4]}$$

$$K_{a2} = 2.0 \times 10^{-6} = \frac{[H_3O^+][C_3H_2O_4^{2-}]}{[HC_3H_2O_4^-]}$$

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



0.200 - x

x

x

$$K_{a1} = 1.4 \times 10^{-3} = \frac{[H_3O^+][HC_3H_2O_4^-]}{[H_2C_3H_2O_4]}$$

$$K_{a1} = 1.4 \times 10^{-3} = \frac{(x)(x)}{(0.200 - x)} \quad \text{Assume } x \text{ is small compared to } 0.200.$$

$$K_{a1} = 1.4 \times 10^{-3} = \frac{(x)(x)}{(0.200)}$$

$$x = 0.016733$$

Check assumption: $(0.016733/0.200) \times 100\% = 8\%$ 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 0.200, and it is necessary to use the quadratic equation.

$$x^2 = 2.8 \times 10^{-4} - 1.4 \times 10^{-3} x$$

$$x^2 + 1.4 \times 10^{-3} x - 2.8 \times 10^{-4} = 0$$

$$a = 1 \quad b = 1.4 \times 10^{-3} \quad c = -2.8 \times 10^{-4}$$

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

$$x = \frac{-1.4 \times 10^{-3} \pm \sqrt{(1.4 \times 10^{-3})^2 - 4(1)(-2.8 \times 10^{-4})}}{2(1)}$$

$$x = 1.6048 \times 10^{-2}$$

$$[H_3O^+] = [HC_3H_2O_4^-] = x = \mathbf{1.6 \times 10^{-2} M}$$

$$pH = -\log [H_3O^+] = -\log (1.6048 \times 10^{-2}) = 1.79458 = \mathbf{1.79}$$

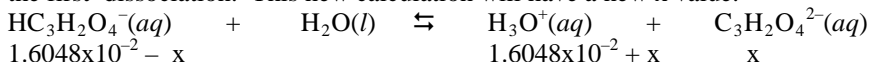
$$[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(1.6048 \times 10^{-2}) = 6.23131 \times 10^{-13} = \mathbf{6.2 \times 10^{-13} M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (6.23131 \times 10^{-13}) = 12.2054 = \mathbf{12.21}$$

$$[\text{H}_2\text{C}_3\text{H}_2\text{O}_4] = (0.200 - 1.6048 \times 10^{-2}) M = 0.183952 = \mathbf{0.18 M}$$

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

Calculate $[\text{C}_3\text{H}_2\text{O}_4^{2-}]$ by using the K_{a2} expression and assuming that $[\text{HC}_3\text{H}_2\text{O}_4^-]$ and $[\text{H}_3\text{O}^+]$ come mostly from the first dissociation. This new calculation will have a new x value.



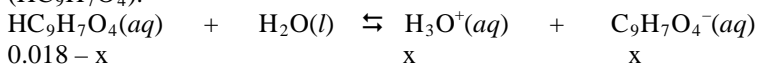
$$K_{a2} = 2.0 \times 10^{-6} = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_2\text{O}_4^{2-}]}{[\text{HC}_3\text{H}_2\text{O}_4^-]}$$

$$K_{a2} = 2.0 \times 10^{-6} = \frac{(1.6048 \times 10^{-2} + x)(x)}{(1.6048 \times 10^{-2} - x)} \quad \text{Assume } x \text{ is small compared to } 1.6048 \times 10^{-2}.$$

$$K_{a2} = 2.0 \times 10^{-6} = \frac{(1.6048 \times 10^{-2})(x)}{(1.6048 \times 10^{-2})}$$

$$x = [\text{C}_3\text{H}_2\text{O}_4^{2-}] = 2.0 \times 10^{-5} = \mathbf{2.0 \times 10^{-5} M}$$

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



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

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

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

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

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

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.018, and it is necessary to use the quadratic equation.

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

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

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

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

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

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

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

- 18.83 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	$\text{HCOOH}(aq)$	$+ \text{H}_2\text{O}(l)$	\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

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

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

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

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

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

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

- 18.84 Electronegativity increases left to right across a period. As the nonmetal becomes more electronegative, the acidity of the binary hydride increases. The electronegative nonmetal attracts the electrons more strongly in the polar bond, shifting the electron density away from H^+ and making the H^+ more easily transferred to a surrounding water molecule to make H_3O^+ .
- 18.85 As the nonmetal increases in size, its bond to hydrogen becomes longer and weaker, so that H^+ is more easily lost, and a stronger acid results.
- 18.86 There is an inverse relationship between the strength of the bond to the acidic proton and the strength of the acid. A weak bond means the hydrogen ion is more easily lost, and hence the acid is stronger.
- 18.87 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.
- 18.88 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.

- 18.89 a) H_2Se b) H_2SO_4 c) H_2SO_3

- 18.90 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) H_2Se , hydrogen selenide, is a stronger acid than H_3As , arsenic hydride, because Se is more electronegative than As.
b) $\text{B}(\text{OH})_3$, boric acid also written as H_3BO_3 , is a stronger acid than $\text{Al}(\text{OH})_3$, aluminum hydroxide, because boron is more electronegative than aluminum.

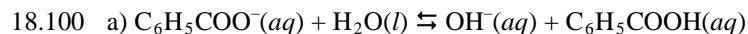
- c) **HBrO₂**, bromous acid, is a stronger acid than HBrO, hypobromous acid, because there are more oxygen atoms in HBrO₂ than in HBrO.
- 18.91 a) **HBr** b) **H₃AsO₄** c) **HNO₂**
- 18.92 Plan: Acidity increases as the value of K_a increases. Determine the ion formed from each salt and compare the 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 M 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 $K_a(\text{Sn}^{2+}) > K_a(\text{Zn}^{2+})$, **0.3 M SnCl₂** is the stronger acid and would have the lower pH.
- 18.93 a) **FeCl₃** b) **BeCl₂**
- 18.94 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}).
- 18.95 a) **NaCl** b) **Co(NO₃)₂**
- 18.96 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an H⁺ and allows the base to act as a proton-acceptor.
- 18.97 The negative charge and lone pair of the anion in many cases is able to extract a proton from water forming OH⁻ ions. Non-basic anions are from strong acids and include I⁻, NO₃⁻, Cl⁻, ClO₄⁻.
- 18.98 a) The species present are: **CH₃COOH(aq), CH₃COO⁻(aq), H₃O⁺(aq), and OH⁻(aq).**
 b) $\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq)$
 The solution is acidic because H₃O⁺ ions are formed.
 $\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{CH}_3\text{COOH}(aq)$
 The solution is basic because OH⁻ ions are formed.
- 18.99 Plan: K_b is the equilibrium constant for a base dissociation which has the generic equation
- $$\text{B}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq). \text{ The } K_b \text{ expression is } \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} . [\text{H}_2\text{O}] \text{ is treated as a constant}$$
- and omitted from the expression. Write the base-dissociation reaction for each base, showing the base accepting a proton from water, and then write the K_b expression.
- Solution:
 a) $\text{C}_5\text{H}_5\text{N}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+(aq) + \text{OH}^-(aq)$

$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

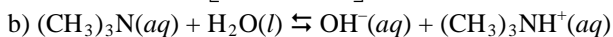
 b) $\text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCO}_3^-(aq) + \text{OH}^-(aq)$

$$K_b = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

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

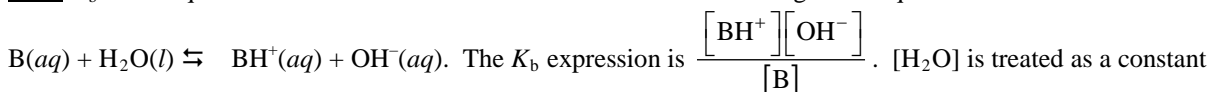


$$K_b = \frac{[\text{C}_6\text{H}_5\text{COOH}][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{COO}^-]}$$



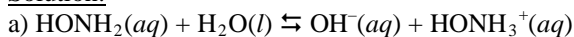
$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$

18.101 Plan: K_b is the equilibrium constant for a base dissociation which has the generic equation

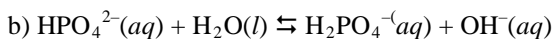


and omitted from the expression. Write the base-dissociation reaction for each base, showing the base accepting a proton from water, and then write the K_b expression.

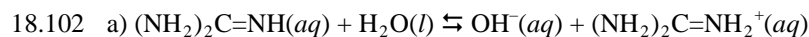
Solution:



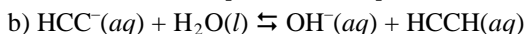
$$K_b = \frac{[\text{HONH}_3^+][\text{OH}^-]}{[\text{HONH}_2]}$$



$$K_b = \frac{[\text{H}_2\text{PO}_4^-][\text{OH}^-]}{[\text{HPO}_4^{2-}]}$$



$$K_b = \frac{[(\text{H}_2\text{N})_2\text{CNH}_2^+][\text{OH}^-]}{[(\text{H}_2\text{N})_2\text{CNH}]}$$

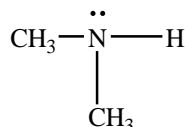


$$K_b = \frac{[\text{HCCH}][\text{OH}^-]}{[\text{HCC}^-]}$$

18.103 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.

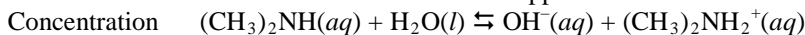
Solution:

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



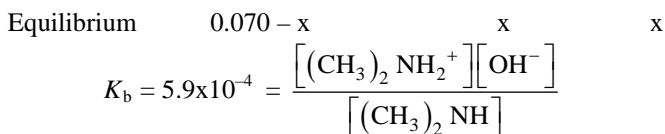
The nitrogen has a lone pair of electrons that will accept the proton from water in the base-dissociation reaction:

The value for the dissociation constant is from Appendix C.



Initial 0.070 0 0

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



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

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

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

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.

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

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

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

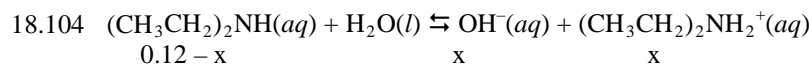
$$a = 1 \quad b = 5.9 \times 10^{-4} \quad c = -4.13 \times 10^{-5}$$

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

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

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

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



$$0.12 - x \quad x \quad x$$

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

$$K_b = 8.6 \times 10^{-4} = \frac{[x][x]}{[0.12 - x]} \quad \text{Assume } x \text{ is small compared to } 0.12.$$

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

$$x = 0.0101587$$

Check assumption: $(0.0101587/0.12) \times 100\% = 8\%$ 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 0.12, and it is necessary to use the quadratic equation.

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

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

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

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

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

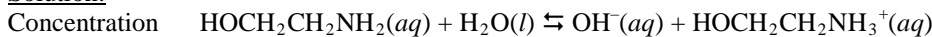
$$x = 9.7378 \times 10^{-3} \text{ M OH}^-$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (9.7378 \times 10^{-3}) = 1.02693 \times 10^{-12} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.02693 \times 10^{-12}) = 11.98846 = \mathbf{11.99}$$

- 18.105 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:



$$\text{Initial} \quad \quad \quad 0.25 \quad \quad \quad 0 \quad \quad \quad 0$$

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

$$\text{Equilibrium} \quad \quad \quad 0.25 - x \quad \quad \quad x \quad \quad \quad x$$

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

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

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

$$x = 2.8284 \times 10^{-3} \text{ M OH}^-$$

Check assumption that x is small compared to 0.25:

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{2.8284 \times 10^{-3}} = 3.535568 \times 10^{-12} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.535568 \times 10^{-12}) = 11.4515 = \mathbf{11.45}$$

- 18.106 $\text{C}_6\text{H}_5\text{NH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{C}_6\text{H}_5\text{NH}_3^+(aq)$

$$\begin{array}{ccc} 0.26 - x & & x \\ & \rightleftharpoons & \\ & & x \end{array}$$

$$K_b = 4.0 \times 10^{-10} = \frac{[\text{C}_6\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_6\text{H}_5\text{NH}_2]}$$

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

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

$$x = 1.01980 \times 10^{-5} \text{ M OH}^-$$

Check assumption: $(1.01980 \times 10^{-5} / 0.26) \times 100\% = 0.004\%$ error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.01980 \times 10^{-5}) = 9.80584 \times 10^{-10} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.80584 \times 10^{-10}) = 9.008515 = \mathbf{9.01}$$

- 18.107 Plan: The K_b of a conjugate base is related to the K_a of the conjugate acid through the equation $K_w = K_a \times K_b$.

Solution:

a) Acetate ion, CH_3COO^- , is the conjugate base of acetic acid, CH_3COOH .

$$K_w = K_a \times K_b$$

$$K_b \text{ of } \text{CH}_3\text{COO}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.55556 \times 10^{-10} = \mathbf{5.6 \times 10^{-10}}$$

b) Anilinium ion is the conjugate acid of the weak base aniline, $\text{C}_6\text{H}_5\text{NH}_2$.

$$K_a \text{ of } \text{C}_6\text{H}_5\text{NH}_3^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-10}} = \mathbf{2.5 \times 10^{-5}}$$

18.108 a) Benzoate ion, $\text{C}_6\text{H}_5\text{COO}^-$, is the conjugate base of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$. The K_b for benzoate ion is related to the K_a for benzoic acid through the equation $K_w = K_a \times K_b$.

$$K_b \text{ of } \text{C}_6\text{H}_5\text{COO}^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.3 \times 10^{-5}} = 1.58730 \times 10^{-10} = \mathbf{1.6 \times 10^{-10}}$$

b) The 2-hydroxyethylammonium ion is the conjugate acid of 2-hydroxyethylamine so the $\text{p}K_a$ for 2-hydroxyethylammonium ion is related to the $\text{p}K_b$ of 2-hydroxyethylamine by the relationship

$$14.00 = \text{p}K_a + \text{p}K_b. \quad \text{The } K_a \text{ may be calculated from the } \text{p}K_a.$$

$$14.00 = \text{p}K_a + \text{p}K_b$$

$$14.00 = \text{p}K_a + 4.49$$

$$\text{p}K_a = 14.00 - 4.49 = 9.51$$

$$K_a = 10^{-\text{p}K_a} = 10^{-9.51} = 3.090295 \times 10^{-10} = \mathbf{3.1 \times 10^{-10}}$$

18.109 Plan: The K_b of a conjugate base is related to the K_a of the conjugate acid through the equation $K_w = K_a \times K_b$.

Solution:

a) HClO_2 is the conjugate acid of chlorite ion, ClO_2^- .

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

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

b) $(\text{CH}_3)_2\text{NH}$ is the conjugate base of $(\text{CH}_3)_2\text{NH}_2^+$.

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

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

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

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

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

The K_b of hydrazine, H_2NNH_2 , is reported in the problem. Hydrazine is the conjugate base of $\text{H}_2\text{N}-\text{NH}_3^+$. The K_a for $\text{H}_2\text{N}-\text{NH}_3^+$ is related to the K_b for H_2NNH_2 through the equation $K_w = K_a \times K_b$, and $\text{p}K_a = -\log K_a$.

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

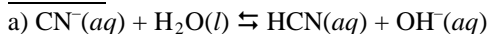
$$\text{p}K_a = -\log(1.17647 \times 10^{-8}) = 7.9294 = \mathbf{7.93}$$

18.111 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 $[\text{H}_3\text{O}^+]$. 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 (M)	$\text{CN}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCN}(aq)$	+	$\text{OH}^-(aq)$
Initial	0.150		—		0		0
Change	-x				+x		+x
Equilibrium	$0.150 - x$				x		x

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

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

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

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

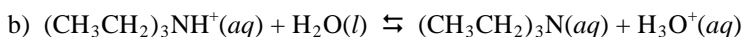
$$x = 1.555 \times 10^{-3} \text{ M OH}^-$$

Check assumption that x is small compared to 0.150:

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

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

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



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

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

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

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

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

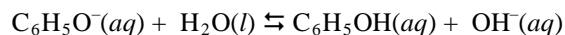
$$[\text{H}_3\text{O}^+] = x = 2.7735 \times 10^{-6} \text{ M}$$

Check assumption that x is small compared to 0.40:

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

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

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



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

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

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

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

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

Assume x is small compared to 0.100.

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

$$x = 3.1622777 \times 10^{-3} \text{ M OH}^-$$

Check assumption: $(3.1622777 \times 10^{-3} / 0.100) \times 100\% = 3\%$ error, so the assumption is valid.

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (3.16227766 \times 10^{-3}) = 3.1622776 \times 10^{-12} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.16227762 \times 10^{-12}) = \mathbf{11.50}$$

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

Concentration (M)	$\text{CH}_3\text{NH}_3^+(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{CH}_3\text{NH}_2(aq)$	$+$	$\text{H}_3\text{O}^+(aq)$
Initial	0.15		—		0		0
Change	-x				+x		+x
Equilibrium	$0.15 - x$				x		x

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

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

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

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

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

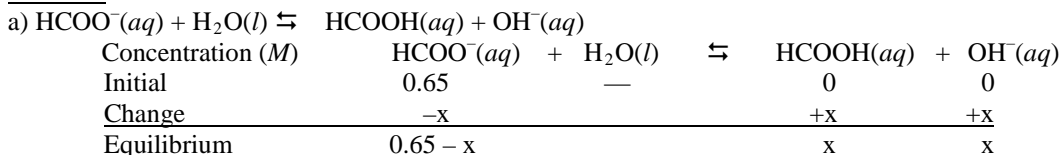
Check assumption: $(1.84637 \times 10^{-6} / 0.15) \times 100\% = 0.001\%$ error, so the assumption is valid.

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

- 18.113 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:



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

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

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

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

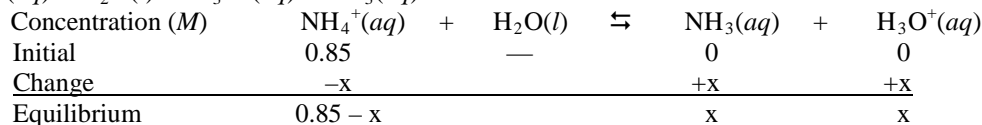
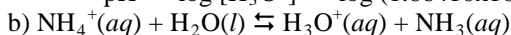
$$x = 6.00925 \times 10^{-6} \text{ M OH}^-$$

Check assumption that x is small compared to 0.65:

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{6.00925 \times 10^{-6}} = 1.66410 \times 10^{-9} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.66410 \times 10^{-9}) = 8.7788 = \mathbf{8.78}$$



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

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

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

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

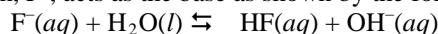
$$[\text{H}_3\text{O}^+] = x = 2.1976 \times 10^{-5} \text{ M}$$

Check assumption that x is small compared to 0.85:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.1976 \times 10^{-5}) = 4.65805 = \mathbf{4.66}$$

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



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

Concentration (M)	$F^-(aq)$	+	$H_2O(l)$	\rightleftharpoons	$HF(aq)$	+	$OH^-(aq)$
Initial	0.75		—		0		0
Change	-x				+x		+x
Equilibrium	$0.75 - x$				x		x

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

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

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

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

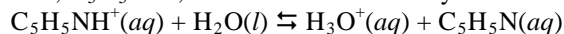
$$x = 3.3210558 \times 10^{-6} \text{ M } OH^-$$

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

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

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

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



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

Concentration (M)	$C_5H_5NH^+(aq)$	+	$H_2O(l)$	\rightleftharpoons	$C_5H_5N(aq)$	+	$H_3O^+(aq)$
Initial	0.88		—		0		0
Change	-x				+x		+x
Equilibrium	$0.88 - x$				x		x

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.88235 \times 10^{-6}$$

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

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

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

$$[H_3O^+] = x = 2.275186 \times 10^{-3} \text{ M}$$

Check assumption: $(2.275186 \times 10^{-3} / 0.88) \times 100\% = 0.3\%$ error, so the assumption is valid.

$$pH = -\log [H_3O^+] = -\log (2.275186 \times 10^{-3}) = 2.64298 = \mathbf{2.64}$$

18.115 Plan: First, calculate the initial molarity 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:

$$\begin{aligned} \text{Molarity of } ClO^- &= \left(\frac{1 \text{ mL solution}}{10^{-3} \text{ L solution}} \right) \left(\frac{1.0 \text{ g solution}}{1 \text{ mL solution}} \right) \left(\frac{6.5\% \text{ NaClO}}{100\% \text{ Solution}} \right) \left(\frac{1 \text{ mol NaClO}}{74.44 \text{ g NaClO}} \right) \left(\frac{1 \text{ mol } ClO^-}{1 \text{ mol NaClO}} \right) \\ &= 0.873186 \text{ M } ClO^- \end{aligned}$$

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

Concentration (M)	$\text{ClO}^-(aq)$	+	$\text{H}_2\text{O}(l)$	\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.

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

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

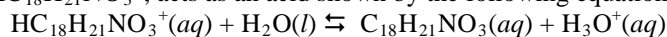
Check assumption that x is small compared to 0.873186:

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

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

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

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



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

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

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

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

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

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

Assume x is small compared to 0.050.

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

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

Check assumption: $(1.7761737 \times 10^{-5}/0.050) \times 100\% = 0.04\% \text{ error, so the assumption is valid.}$

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

18.117 Salts that contain anions of weak acids and cations of strong bases are basic. Salts that contain cations of weak bases or small, highly charged metal cations, and anions of strong acids are acidic. Salts that contain cations of strong bases and anions of strong acids are neutral.

Basic salt: KCN (K^+ is the cation from the strong base KOH; CN^- is the anion from the weak acid, HCN.)

Acid salt: FeCl_3 or NH_4NO_3 (Fe^{3+} is a small, highly charged metal cation and Cl^- is the anion of the strong acid HCl; NH_4^+ is the cation of the weak base NH_3 , while NO_3^- is the anion of the strong acid HNO_3 .)

Neutral salt: KNO_3 (K^+ is the cation of the strong base KOH, while NO_3^- is the anion of the strong acid HNO_3 .)

- 18.118 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:

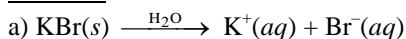


Sodium chloride, NaCl, is the salt of a strong base, NaOH, and strong acid, HCl. This combination yields a salt that is neutral in aqueous solution as neither Na⁺ or Cl⁻ react in water to change the [H₃O⁺].

- 18.119 If K_a for the conjugate acid of the anion is approximately equal to K_b for the conjugate base of the cation, the solution will be close to neutral. Otherwise, the solution will be acidic or basic. In this case, the K_a for the conjugate acid (CH₃COOH) is 1.8x10⁻⁵, and the K_b for the conjugate base (NH₃) is 1.76x10⁻⁵.

- 18.120 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.

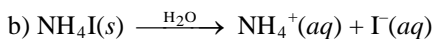
Solution:



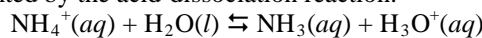
K⁺ is the conjugate acid of a strong base, so it does not influence pH.

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.

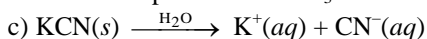


NH₄⁺ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H₃O⁺ as represented by the acid-dissociation reaction:



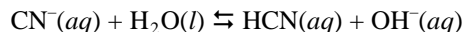
I⁻ is the conjugate base of a strong acid, so it will not influence the pH.

The production of H₃O⁺ from the ammonium ion makes the solution of NH₄I **acidic**.

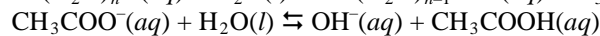
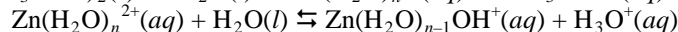
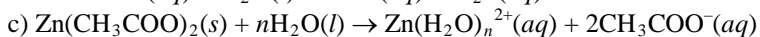
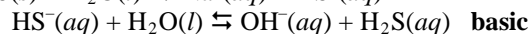
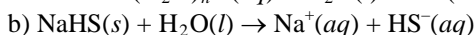
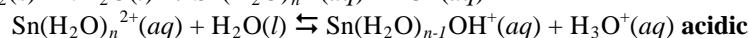
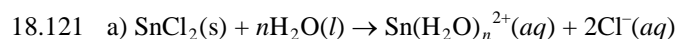


K⁺ is the conjugate acid of a strong base, so it does not influence pH.

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**.



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

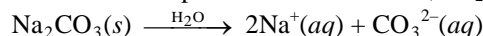
$$K_b(\text{CH}_3\text{COO}^-) = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.5556 \times 10^{-10}$$

The two K values are similar, so the solution is close to **neutral or slightly acidic**.

- 18.122 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:

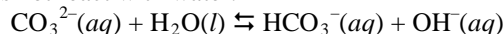
- a) The two ions that comprise sodium carbonate, Na₂CO₃, are sodium ion, Na⁺, and carbonate ion, CO₃²⁻.



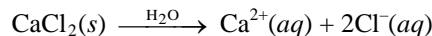
Sodium ion is derived from the strong base NaOH. Carbonate ion is derived from the weak acid HCO₃⁻.

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, CaCl₂, are calcium ion, Ca²⁺, and chloride ion, Cl⁻.

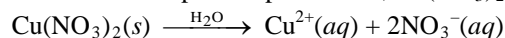


Calcium ion is derived from the strong base $\text{Ca}(\text{OH})_2$. Chloride ion is derived from the strong acid HCl .

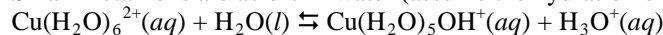
A salt derived from a strong base and strong acid produces a **neutral** solution.

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^- .

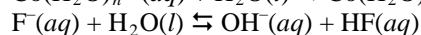
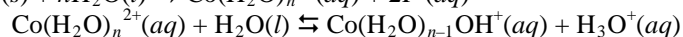
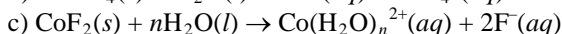
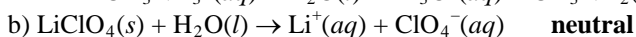
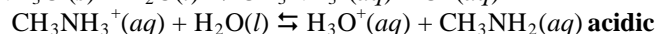
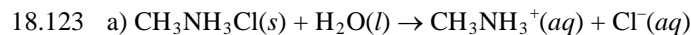


Small metal ions are acidic in water (assume the hydration of Cu^{2+} is 6):



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**.

solution



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

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

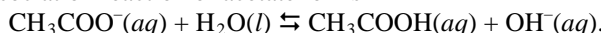
The two K values are similar so the solution is close to **neutral or slightly acidic**.

- 18.124 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.

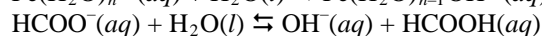
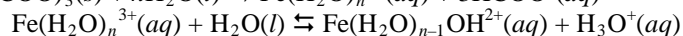
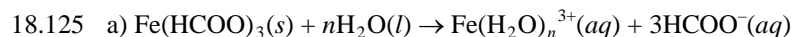
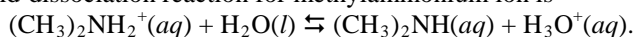
Solution:

- Br^- 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 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



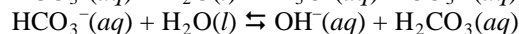
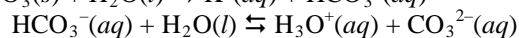
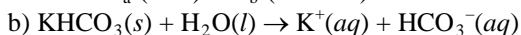
c) A solution of dimethylammonium bromide is **acidic** because $(\text{CH}_3)_2\text{NH}_2^+$ is the conjugate acid of a weak base and therefore forms H_3O^+ in solution whereas Br^- is the conjugate base of a strong acid and does not influence the pH of the solution. The acid-dissociation reaction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



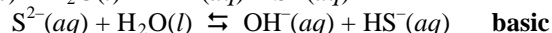
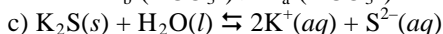
$$K_a(\text{Fe}^{3+}) = 6 \times 10^{-3}$$

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

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



$$K_b(\text{HCO}_3^-) > K_a(\text{HCO}_3^-) \quad \text{basic}$$



- 18.126 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:

- phosphate a) The two ions that comprise ammonium phosphate, $(\text{NH}_4)_3\text{PO}_4$, are the ammonium ion, NH_4^+ , and the ion, PO_4^{3-} .
- $$\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq) \quad K_a = K_w/K_b(\text{NH}_3) = 5.7 \times 10^{-10}$$
- $$\text{PO}_4^{3-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{OH}^-(aq) \quad K_b = K_w/K_{a3}(\text{H}_3\text{PO}_4) = 2.4 \times 10^{-2}$$
- A comparison of K_a and K_b is necessary since both ions are derived from a weak base and weak acid. The K_a of NH_4^+ is determined by using the K_b of its conjugate base, NH_3 (Appendix). The K_b of PO_4^{3-} is determined by using the K_a of its conjugate acid, HPO_4^{2-} . The K_a of HPO_4^{2-} comes from K_{a3} of H_3PO_4 (Appendix). Since $K_b > K_a$, a solution of $(\text{NH}_4)_3\text{PO}_4$ is **basic**.
- H_3PO_4 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^- .
- $$\text{SO}_4^{2-}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HSO}_4^-(aq) + \text{OH}^-(aq)$$
- A solution of sodium sulfate is **basic**.
- c) The two ions that comprise lithium hypochlorite, LiClO , are lithium ion, Li^+ , and hypochlorite ion, ClO^- . Lithium ion is derived from the strong base LiOH . Hypochlorite ion is derived from the weak acid, HClO (hypochlorous acid).
- $$\text{ClO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HClO}(aq) + \text{OH}^-(aq)$$
- A solution of lithium hypochlorite is **basic**.

- 18.127 a) $\text{Pb}(\text{CH}_3\text{COO})_2(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Pb}(\text{H}_2\text{O})_n^{2+}(aq) + 2\text{CH}_3\text{COO}^-(aq)$
- $$\text{Pb}(\text{H}_2\text{O})_n^{2+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Pb}(\text{H}_2\text{O})_{n-1}\text{OH}^+(aq) + \text{H}_3\text{O}^+(aq)$$
- $$K_a(\text{Pb}^{2+}) = 3 \times 10^{-8}$$
- $$\text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq)$$
- $$K_b(\text{CH}_3\text{COO}^-) = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.5556 \times 10^{-10}$$
- $$K_a(\text{Pb}^{2+}) > K_b(\text{CH}_3\text{COO}^-) \quad \text{acidic}$$
- b) $\text{Cr}(\text{NO}_2)_3(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + 3\text{NO}_2^-(aq)$
- $$\text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cr}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}(aq) + \text{H}_3\text{O}^+(aq)$$
- $$\text{NO}_2^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HNO}_2(aq)$$
- $$K_a(\text{Cr}^{3+}) = 1 \times 10^{-4}$$
- $$K_b(\text{NO}_2^-) = K_w/K_a = (1.0 \times 10^{-14})/(7.1 \times 10^{-4}) = 1.40845 \times 10^{-11}$$
- $$K_a(\text{Cr}^{3+}) > K_b(\text{NO}_2^-) \quad \text{acidic}$$
- c) $\text{CsI}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Cs}^+(aq) + \text{I}^-(aq) \quad \text{neutral}$

- 18.128 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)

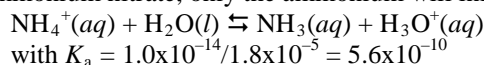
Iron(II) nitrate, $\text{Fe}(\text{NO}_3)_2$, is an acidic solution because the iron ion is a small, highly charged metal ion that acts as a weak acid and nitrate ion is the conjugate base of a strong acid, so it does not influence pH.

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: **$\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$**

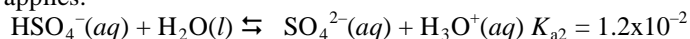
In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:



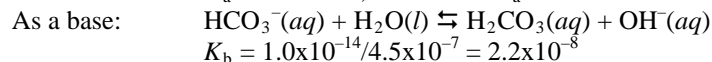
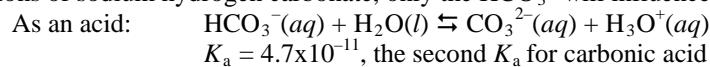
Therefore, the solution of ammonium nitrate is acidic.

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:

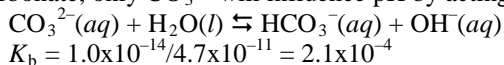


In solutions of sodium hydrogen carbonate, only the HCO_3^- will influence pH and it, like HSO_4^- , is amphoteric:



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:



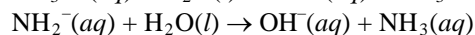
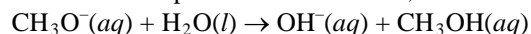
Therefore, the solution of sodium carbonate is basic.

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.

- 18.129 a) $\text{KClO}_2 > \text{MgCl}_2 > \text{FeCl}_2 > \text{FeCl}_3$
 b) $\text{NaBrO}_2 > \text{NaClO}_2 > \text{NaBr} > \text{NH}_4\text{Br}$

- 18.130 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.



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

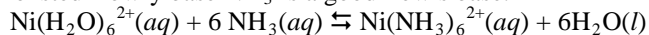
- 18.132 Ammonia, NH_3 , is a more basic solvent than H_2O . In a more basic solvent, weak acids like HF act like strong acids and are 100% dissociated.

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

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

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

- 18.135 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, the following equation shows that the weak Brønsted-Lowry base NH_3 is a good Lewis base.



b) The **cyanide ion** has a lone pair to donate from either the C or the N, and donates an electron pair to the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex. It is the Lewis base for the forward direction of this reaction. In the reverse direction, **water** donates one of the electron pairs on the oxygen to the $\text{Cu}(\text{CN})_4^{2-}$ and is the Lewis base.

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

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

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

18.138 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.

- 18.139 a) **Lewis acid** b) **Lewis base** c) **Lewis base** d) **Lewis acid**

18.140 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:

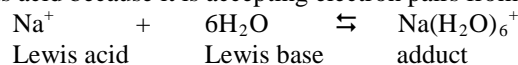
- a) The boron atom in boron trifluoride, BF_3 , is electron deficient (has six electrons instead of eight) and can accept an electron pair; it is a **Lewis acid**.
 b) The sulfide ion, S^{2-} , can donate any of four electron pairs and is a **Lewis base**.
 c) The Lewis dot structure for the sulfite 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**.

- 18.141 a) **Lewis acid** b) **Lewis base** c) **Lewis acid** d) **Lewis acid**

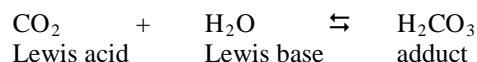
18.142 Plan: A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

Solution:

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



- 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_3 . The fluoride ion is the Lewis base and the boron trifluoride is the Lewis acid.



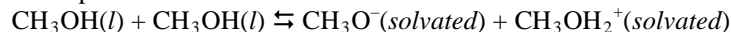
- 18.143 a) $\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}_3\text{O}^+$
 Lewis acid Lewis base
 b) $\text{H}_2\text{O} + \text{H}^- \rightleftharpoons \text{OH}^- + \text{H}_2$
 Lewis acid Lewis base
 c) $4\text{CO} + \text{Ni} \rightleftharpoons \text{Ni}(\text{CO})_4$
 Lewis base Lewis acid

18.144 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:

Range: 5.2×10^{-7} to $6.6 \times 10^{-7} M OH^-$

- 18.148 a) Acids will vary in the amount they dissociate (acid strength) depending on the acid-base character of the solvent. Water and methanol have different acid-base characters.
 b) The K_a is the measure of an acid's strength. A stronger acid has a smaller pK_a . Therefore, phenol is a stronger acid in water than it is in methanol. In other words, water more readily accepts a proton from phenol than does methanol, i.e., methanol is a weaker base than water.
 c) $C_6H_5OH(solvent) + CH_3OH(l) \rightleftharpoons CH_3OH_2^+(solvent) + C_6H_5O^-(solvent)$
 The term "solvent" 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.

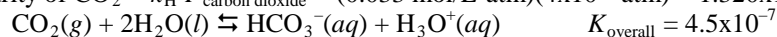


In this equation "(solvent)" indicates that the molecules are solvated by methanol.

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

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

- 18.149 a) *Step 1* $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ **Lewis**
Step 2 $H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$ **Brønsted-Lowry and Lewis**
 b) Molarity of $CO_2 = k_H P_{\text{carbon dioxide}} = (0.033 \text{ mol/L}\cdot\text{atm})(4 \times 10^{-4} \text{ atm}) = 1.320 \times 10^{-5} M CO_2$



$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[H_3O^+][HCO_3^-]}{[CO_2]}$$

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{[1.320 \times 10^{-5} - x]}$$

Assume x is small compared to

1.320×10^{-5} .

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{1.320 \times 10^{-5}}$$

$$x = 2.4372 \times 10^{-6}$$

Check assumption that x is small compared to 1.320×10^{-5} :

$$\frac{2.4372 \times 10^{-6}}{1.320 \times 10^{-5}}(100) = 18\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 1.320×10^{-5} , and it is necessary to use the quadratic equation.

$$x^2 = (4.5 \times 10^{-7})(1.320 \times 10^{-5} - x) = 5.940 \times 10^{-12} - 4.5 \times 10^{-7}x$$

$$x^2 + 4.5 \times 10^{-7}x - 5.940 \times 10^{-12} = 0$$

$$a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -5.940 \times 10^{-12}$$

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

$$x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-5.940 \times 10^{-12})}}{2(1)}$$

$$x = 2.222575 \times 10^{-6} M H_3O^+$$

$$pH = -\log [H_3O^+] = -\log (2.222575 \times 10^{-6}) = 5.6531 = \mathbf{5.6}$$

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

$$K_a = 4.7 \times 10^{-11} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

Use the unrounded x from part b).

$$K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{[2.222575 \times 10^{-6} + x][x]}{[2.222575 \times 10^{-6} - x]} \quad \text{Assume } x \text{ is small compared to } 2 \times 10^{-6}.$$

$$K_{\text{overall}} = 4.5 \times 10^{-11} = \frac{[2.222575 \times 10^{-6}][x]}{[2.222575 \times 10^{-6}]}$$

$$[\text{CO}_3^{2-}] = x = 4.5 \times 10^{-11} = \mathbf{5 \times 10^{-11} M \text{ CO}_3^{2-}}$$

Check assumption that x is small compared to 2×10^{-6} :

$$\frac{4.5 \times 10^{-11}}{2 \times 10^{-6}}(100) = 0.0023\% \text{ error, so the assumption is valid.}$$

d) New molarity of $\text{CO}_2 = 2k_{\text{H}} P_{\text{carbon dioxide}} = 2(0.033 \text{ mol/L}\cdot\text{atm})(4 \times 10^{-4} \text{ atm}) = 2.640 \times 10^{-5} M \text{ CO}_2$

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

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{[2.640 \times 10^{-5} - x]}$$

Assume x is small compared to 2.640×10^{-5} .

$$K_{\text{overall}} = 4.5 \times 10^{-7} = \frac{[x][x]}{[2.640 \times 10^{-5}]}$$

$$x = 3.44674 \times 10^{-6}$$

Check assumption that x is small compared to 2.640×10^{-5} :

$$\frac{3.44674 \times 10^{-6}}{2.640 \times 10^{-5}}(100) = 13\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 2.640×10^{-5} , and it is necessary to use the quadratic equation.

$$x^2 = (4.5 \times 10^{-7})(2.640 \times 10^{-5} - x) = 1.1880 \times 10^{-11} - 4.5 \times 10^{-7} x$$

$$x^2 + 4.5 \times 10^{-7} x - 1.1880 \times 10^{-11} = 0$$

$$a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -1.1880 \times 10^{-11}$$

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

$$x = \frac{-4.5 \times 10^{-7} \pm \sqrt{(4.5 \times 10^{-7})^2 - 4(1)(-1.1880 \times 10^{-11})}}{2(1)}$$

$$x = 3.229 \times 10^{-6} M \text{ H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.229 \times 10^{-6}) = 5.4909 = \mathbf{5.5}$$

18.150 At great depths, the higher pressure increases the concentration of H_3O^+ and the effect is to shift the dissolving reaction to the right, so seashells dissolve more rapidly.

18.151 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 $(\text{CH}_3)_3\text{N}$, the Lewis base.

b) Tin is the element in the Lewis acid accepting the electron pair. The electron configuration of tin is $[\text{Kr}]5s^2 4d^{10} 5p^2$. The four bonds to tin are formed by sp^3 hybrid orbitals, which completely fill the $5s$ and $5p$ orbitals. The $5d$ orbitals are empty and available for the bond with trimethylamine.

18.152 Plan: A 10-fold dilution means that the chemist takes 1 mL of the $1.0 \times 10^{-5} M$ solution and dilutes it to 10 mL (or dilute 10 mL to 100 mL). The chemist then dilutes the diluted solution in a 1:10 ratio, and repeats this process for the next two successive dilutions. $M_1 V_1 = M_2 V_2$ can be used to find the molarity after each dilution. After each dilution, find $[\text{H}_3\text{O}^+]$ and calculate the pH.

Solution:

Hydrochloric acid is a strong acid that completely dissociates in water. Therefore, the concentration of H_3O^+ is the same as the starting acid concentration: $[\text{H}_3\text{O}^+] = [\text{HCl}]$. The original solution pH:

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

Dilution 1: $M_1 V_1 = M_2 V_2$

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

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-6} \text{ M } \text{H}_3\text{O}^+$$

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

Dilution 2:

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

$$[\text{H}_3\text{O}^+]_{\text{HCl}} = 1.0 \times 10^{-7} \text{ M } \text{H}_3\text{O}^+$$

Once the concentration of strong acid is close to the concentration of H_3O^+ from water autoionization, the $[\text{H}_3\text{O}^+]$ in the solution does not equal the initial concentration of the strong acid. The calculation of $[\text{H}_3\text{O}^+]$ must be based on the water ionization equilibrium:



The dilution gives an initial $[\text{H}_3\text{O}^+]$ of $1.0 \times 10^{-7} \text{ M}$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (M)	$2\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$
Initial	—		1×10^{-7}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-7} + x$		x

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

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

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

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

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

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-7} + x) \text{ M} = (1.0 \times 10^{-7} + 6.18034 \times 10^{-8}) \text{ M} = 1.618034 \times 10^{-7} \text{ M } \text{H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.618034 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$$

Dilution 3:

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

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

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

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

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

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

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

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

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

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

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

Dilution 4:

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

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

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

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

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) M = 1.005012 \times 10^{-7} M \text{ H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.005012 \times 10^{-7}) = 6.9978 = \mathbf{7.00}$$

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.

18.153 a) **Steps 1, 2, and 4** are Lewis acid-base reactions.

b) *Step 1* $\text{Cl}_2 + \text{FeCl}_3 \rightleftharpoons \text{FeCl}_5$ (or $\text{Cl}^+\text{FeCl}_4^-$)

Lewis acid = FeCl₃ **Lewis base = Cl₂**

Step 2 $\text{C}_6\text{H}_6 + \text{Cl}^+\text{FeCl}_4^- \rightleftharpoons \text{C}_6\text{H}_6\text{Cl}^+ + \text{FeCl}_4^-$

Lewis acid = C₆H₆ **Lewis base = Cl⁺FeCl₄⁻**

Step 4 $\text{H}^+ + \text{FeCl}_4^- \rightleftharpoons \text{HCl} + \text{FeCl}_3$

Lewis acid = H⁺ **Lewis base = FeCl₄⁻**

18.154 a) $\text{HY}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{Y}^-(aq)$

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

Concentrations in Beaker A:

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

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

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

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

Concentrations in Beaker B:

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

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

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

Beaker B is not at equilibrium.

Concentrations in Beaker C:

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

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

$$Q = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.066667][0.066667]}{[0.133333]} = 0.0333345 = 0.033$$

Beaker C is not at equilibrium.

Concentrations in Beaker D:

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

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

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

Beaker D is at equilibrium.

b) For both beakers B and C, $Q < K_a$. Therefore, the reaction is proceeding to the **right** to produce more products.

c) Yes, dilution affects the extent of dissociation of a weak acid. Dilution increases the degree of dissociation.

For example, in Beaker A, 4 of 12 HY molecules have dissociated for a $(4/12)100 = 33\%$ dissociation. In Beaker D, 2 of 4 HY molecules have dissociated for a $(2/4)100 = 50\%$ dissociation.

18.155 a) Electrical conductivity of 0.1 M HCl is **higher** than that of 0.1 M CH₃COOH. Conductivity is proportional to the concentration of charge in the solution. Since HCl dissociates to a greater extent than CH₃COOH, the concentration of ions, and thus the charge, is greater in 0.1 M HCl than in 0.1 M CH₃COOH.

b) The electrical conductivity of the two solutions will be **approximately the same** because at low concentrations the autoionization of water is significant causing the concentration of ions, and thus the charge, to be about the same in the two solutions. In addition, the percent dissociation of a weak electrolyte such as acetic acid increases with decreasing concentration.

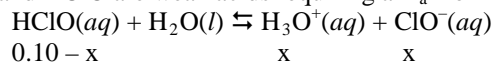
18.156 In step (1), the RCOOH is the Lewis base and the H⁺ is the Lewis acid. In step (2), the RC(OH)₂⁺ is the Lewis acid and the R'OH is the Lewis base.

18.157 a) $\text{pH} = -\log [\text{H}_3\text{O}^+]$

HCl is a strong acid so $[\text{H}_3\text{O}^+] = M \text{ HCl}$

$$\text{pH} = -\log (0.10) = \mathbf{1.00}$$

HClO₂ and HClO are weak acids requiring a K_a from the Appendix.



$$K_a = 2.9 \times 10^{-8} = \frac{[\text{H}_3\text{O}^+][\text{ClO}^-]}{[\text{HClO}]}$$

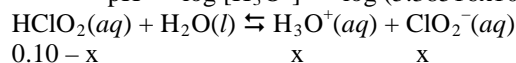
$$K_a = 2.9 \times 10^{-8} = \frac{(x)(x)}{(0.10 - x)} \quad \text{Assume } x \text{ is small compared to } 0.10.$$

$$K_a = 2.9 \times 10^{-8} = \frac{(x)(x)}{(0.10)}$$

$$[\text{H}_3\text{O}^+] = x = 5.38516 \times 10^{-5} \text{ M}$$

Check assumption: $(5.38516 \times 10^{-5} / 0.10) \times 100\% = 0.05\%$. The assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.38516 \times 10^{-5}) = 4.2688 = \mathbf{4.27}$$



$$K_a = 1.1 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]}$$

$$K_a = 1.1 \times 10^{-2} = \frac{[x][x]}{[0.10 - x]} \quad \text{Assume } x \text{ is small compared to } 0.10.$$

$$K_a = 1.1 \times 10^{-2} = \frac{[x][x]}{[0.10]}$$

$$x = 0.033166$$

Check assumption: $(0.033166/0.10) \times 100\% = 33\%$. The assumption is not valid.

The problem will need to be solved as a quadratic.

$$x^2 = (1.1 \times 10^{-2})(0.10 - x) = 1.1 \times 10^{-3} - 1.1 \times 10^{-2} x$$

$$x^2 + 1.1 \times 10^{-2} x - 1.1 \times 10^{-3} = 0$$

$$a = 1 \quad b = 1.1 \times 10^{-2} \quad c = -1.1 \times 10^{-3}$$

$$x = \frac{-1.1 \times 10^{-2} \pm \sqrt{(1.1 \times 10^{-2})^2 - 4(1)(-1.1 \times 10^{-3})}}{2(1)}$$

$$x = 2.8119 \times 10^{-2} M \text{ H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.8119 \times 10^{-2}) = 1.550997 = \mathbf{1.55}$$

b) The lowest H_3O^+ concentration is from the HClO . Leave the HClO beaker alone, and dilute the other acids until they yield the same H_3O^+ concentration. A dilution calculation is needed to calculate the amount of water added.

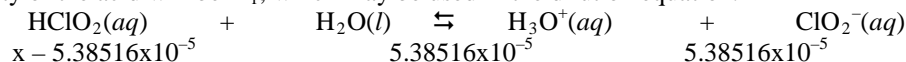
$$\text{HCl} \quad M_i = 0.10 M \quad V_i = 100. \text{ mL} \quad M_f = 5.38516 \times 10^{-5} M \quad V_f = ?$$

$$M_i V_i = M_f V_f$$

$$V_f = M_i V_i / M_f = [(0.10 M)(100. \text{ mL})] / (5.38516 \times 10^{-5} M) = 1.85695 \times 10^5 \text{ mL}$$

$$\text{Volume water added} = (1.85695 \times 10^5 \text{ mL}) - 100. \text{ mL} = 1.85595 \times 10^5 = \mathbf{1.9 \times 10^5 \text{ mL H}_2\text{O added}}$$

HClO_2 requires the K_a for the acid with the ClO_2^- concentration equal to the H_3O^+ concentration. The final molarity of the acid will be M_f , which may be used in the dilution equation.



$$K_a = 1.1 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{ClO}_2^-]}{[\text{HClO}_2]}$$

$$K_a = 1.1 \times 10^{-2} = \frac{[5.38516 \times 10^{-5}][5.38516 \times 10^{-5}]}{[x - 5.38516 \times 10^{-5}]}$$

$$x = M_f = 5.41152 \times 10^{-5} M$$

$$M_i = 0.10 M \quad V_i = 100. \text{ mL} \quad M_f = 5.41152 \times 10^{-5} M \quad V_f = ?$$

$$M_i V_i = M_f V_f$$

$$V_f = M_i V_i / M_f = [(0.10 M)(100. \text{ mL})] / (5.41152 \times 10^{-5} M) = 1.8479 \times 10^5 \text{ mL}$$

$$\text{Volume water added} = (1.8479 \times 10^5 \text{ mL}) - 100. \text{ mL} = 1.8469 \times 10^5 = \mathbf{1.8 \times 10^5 \text{ mL H}_2\text{O added}}$$

18.158 Plan: Determine the hydrogen ion concentration from the pH. The molarity and the volume will give the number of moles, and with the aid of Avogadro's number, the number of ions may be found.

Solution:

$$M \text{ H}_3\text{O}^+ = 10^{-\text{pH}} = 10^{-6.2} = 6.30957 \times 10^{-7} M$$

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

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

18.159 a) $\text{NH}_3(l) \rightleftharpoons \text{NH}_4^+(am) + \text{NH}_2^-(am)$

In this equilibrium "(am)" indicated ammoniated, solvated by ammonia, instead of "(aq)" to indicate aqueous, solvated by water.

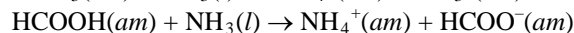
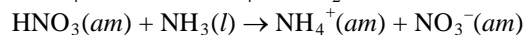
Initially, based on the equilibrium: $K_c = \frac{[\text{NH}_4^+][\text{NH}_2^-]}{[\text{NH}_3]^2}$

Since NH_3 is a liquid and a solvent:

$$K_c [\text{NH}_3]^2 = K_{\text{am}} = [\text{NH}_4^+][\text{NH}_2^-]$$

b) **Strongest acid** = NH_4^+ **Strongest base** = NH_2^-

c) $\text{NH}_2^- > \text{NH}_4^+$: basic $\text{NH}_4^+ > \text{NH}_2^-$: acidic



HNO_3 is a strong acid in water while HCOOH is a weak acid in water. However, both acids are equally strong (i.e., their strengths are leveled) in NH_3 because they dissociate completely to form NH_4^+ .

d) $K_{\text{am}} = [\text{NH}_4^+][\text{NH}_2^-] = 5.1 \times 10^{-27}$

$$[\text{NH}_4^+] = [\text{NH}_2^-] = x$$

$$K_{\text{am}} = [x][x] = 5.1 \times 10^{-27}$$

$$x = 7.1414 \times 10^{-14} = \mathbf{7.1 \times 10^{-14} \text{ M NH}_4^+}$$

e) $2\text{H}_2\text{SO}_4(\text{l}) \rightleftharpoons \text{H}_3\text{SO}_4^+(\text{sa}) + \text{HSO}_4^-(\text{sa})$ (*sa*) = solvated by sulfuric acid (sulf)

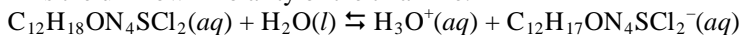
$$K_{\text{sulf}} = [\text{H}_3\text{SO}_4^+][\text{HSO}_4^-] = 2.7 \times 10^{-4}$$

$$[\text{H}_3\text{SO}_4^+] = [\text{HSO}_4^-] = x$$

$$K_{\text{sulf}} = [x][x] = 2.7 \times 10^{-4}$$

$$x = 1.643 \times 10^{-2} = \mathbf{1.6 \times 10^{-2} \text{ M HSO}_4^-}$$

18.160 *M* is the unknown molarity of the thiamine.



$$\begin{array}{ccc} M - x & & x \end{array}$$

pH = 3.50

$$[\text{H}_3\text{O}^+] = 10^{-3.50} = 3.1623 \times 10^{-4} \text{ M} = x$$

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

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

$$K_a = 3.37 \times 10^{-7} = \frac{(3.1623 \times 10^{-4})(3.1623 \times 10^{-4})}{(M - 3.1623 \times 10^{-4})}$$

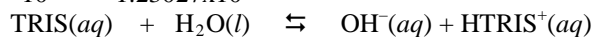
$$M = 0.29705633 \text{ M}$$

$$\begin{aligned} \text{Mass (g)} &= \left(\frac{0.29705633 \text{ mol thiamine HCl}}{\text{L}} \right) \left(\frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) (10.00 \text{ mL}) \left(\frac{337.27 \text{ g thiamine HCl}}{1 \text{ mol thiamine HCl}} \right) \\ &= 1.00188 = 1.0 \text{ g thiamine hydrochloride} \end{aligned}$$

18.161 Plan: Determine K_b using the relationship $K_b = 10^{-\text{pKb}}$. 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:

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



$$\begin{array}{cccc} \text{Initial} & 0.075 & - & 0 & 0 \end{array}$$

$$\begin{array}{cccc} \text{Change} & -x & & +x & +x \end{array}$$

$$\begin{array}{cccc} \text{Equilibrium} & 0.075 - x & & x & x \end{array}$$

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

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

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

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

Check assumption that x is small compared to 0.075:

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.03760 \times 10^{-4}} = 3.292073 \times 10^{-11} \text{ M}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.292073 \times 10^{-11}) = 10.4825 = \mathbf{10.48}$$

- 18.162 $\text{Fe}^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq})$ Lewis acid-base reaction
 $\text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ Brønsted-Lowry acid-base reaction

- 18.163 The pH is dependent on the *molar* concentration of H_3O^+ . Convert % w/v to molarity, and use the K_a of acetic acid to determine $[\text{H}_3\text{O}^+]$ from the equilibrium expression.

Convert % w/v to molarity using the molecular weight of acetic acid (CH_3COOH):

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

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

	$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial	0.832639	—	0 0
Change	-x	+x	+x
Equilibrium	0.832639 - x	x	x

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

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

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

$$x = 3.8714 \times 10^{-3} \text{ M} = [\text{H}_3\text{O}^+]$$

Check assumption: $[3.8714 \times 10^{-3} / 0.832639] \times 100\% = 0.46\%$, therefore the assumption is good.

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.8714 \times 10^{-3}) = 2.412132 = \mathbf{2.41}$$

- 18.164 Plan: When an initial acid concentration is diluted, the percent dissociation of the acid increases.

Solution:

When the solution is diluted, the percent dissociation of the acid HB increases. There is no single correct scene. Any scene in which the total number of $\text{HB} + \text{B}^-$ is less than in the original solution yet the relative number of HB dissociated is greater would be correct. In the original scene, 2 of 12 HB molecules, or 16.7%, have dissociated. One possible scene after dilution could show 8 HB molecules, 2 B^- and 2 H_3O^+ ions. Then the dissociation is 2 $\text{B}^- / 10 \text{ HB} = 20\%$ dissociation.

- 18.165 a) The strong acid solution would have a larger electrical conductivity.
 b) The strong acid solution would have a lower pH.
 c) The strong acid solution would bubble more vigorously.

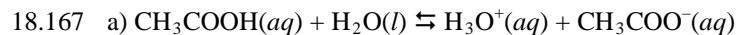
- 18.166 Plan: Assuming that the pH in the specific cellular environment is equal to the optimum pH for the enzyme, the hydronium ion concentrations are $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$.

Solution:

Salivary amylase, mouth: $[\text{H}_3\text{O}^+] = 10^{-6.8} = 1.58489 \times 10^{-7} = \mathbf{2 \times 10^{-7} M}$

Pepsin, stomach: $[\text{H}_3\text{O}^+] = 10^{-2.0} = \mathbf{1 \times 10^{-2} M}$

Trypsin, pancreas: $[\text{H}_3\text{O}^+] = 10^{-9.5} = 3.1623 \times 10^{-10} = \mathbf{3 \times 10^{-10} M}$



$$0.240 - x \qquad \qquad \qquad x \qquad \qquad \qquad x$$

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

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.240 - x)} \quad \text{Assume } x \text{ is small compared to } 0.240.$$

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.240)}$$

$$x = 2.07846 \times 10^{-3}$$

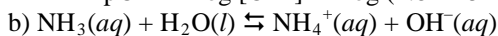
Check assumption: $[2.07846 \times 10^{-3} / 0.240] \times 100\% = 0.9\%$, therefore the assumption is good.

$$x = [\text{H}_3\text{O}^+] = 2.07846 \times 10^{-3} = \mathbf{2.1 \times 10^{-3} M \text{ H}_3\text{O}^+}$$

$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (2.07846 \times 10^{-3}) = 4.81125 \times 10^{-12} = \mathbf{4.8 \times 10^{-12} M \text{ OH}^-}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.07846 \times 10^{-3}) = 2.682258 = \mathbf{2.68}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (4.81125 \times 10^{-12}) = 11.317742 = \mathbf{11.32}$$



$$0.240 - x \qquad \qquad \qquad x \qquad \qquad \qquad x$$

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$K_b = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.240 - x)} \quad \text{Assume } x \text{ is small compared to } 0.240.$$

$$K_b = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.240)}$$

$$x = 2.07846 \times 10^{-3}$$

Check assumption: $[2.07846 \times 10^{-3} / 0.240] \times 100\% = 0.9\%$, therefore the assumption is good.

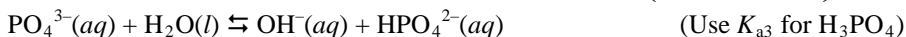
$$x = [\text{OH}^-] = 2.07846 \times 10^{-3} = \mathbf{2.1 \times 10^{-3} M \text{ OH}^-}$$

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (2.07846 \times 10^{-3}) = 4.81125 \times 10^{-12} = \mathbf{4.8 \times 10^{-12} M \text{ H}_3\text{O}^+}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (2.07846 \times 10^{-3}) = 2.682258 = \mathbf{2.68}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (4.81125 \times 10^{-12}) = 11.317742 = \mathbf{11.32}$$

18.168 Concentration = $M = \left(\frac{33 \text{ g Na}_3\text{PO}_4}{1 \text{ L}} \right) \left(\frac{1 \text{ mol Na}_3\text{PO}_4}{163.94 \text{ g Na}_3\text{PO}_4} \right) \left(\frac{1 \text{ mol PO}_4^{3-}}{1 \text{ mol Na}_3\text{PO}_4} \right) = 0.20129 \text{ M PO}_4^{3-}$



$$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (4.2 \times 10^{-13}) = 0.0238095$$

$$K_b = 0.0238095 = \frac{(\text{HPO}_4^{2-})(\text{OH}^-)}{(\text{PO}_4^{3-})}$$

$$K_b = 0.0238095 = \frac{(x)(x)}{(0.20129 - x)}$$

A quadratic is required.

$$x^2 + 0.0238095x - 0.00479261 = 0$$

$$a = 1 \quad b = 0.0238095 \quad c = -0.00479261$$

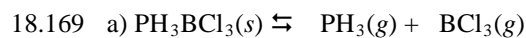
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.0238095 \pm \sqrt{(0.0238095)^2 - 4(1)(-0.00479261)}}{2(1)}$$

$$x = 0.058340 = \mathbf{0.058 M OH^-}$$

$$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(0.058340) = 1.7140898 \times 10^{-13} M H_3O^+$$

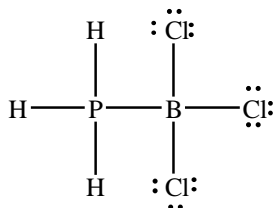
$$pH = -\log [H_3O^+] = -\log (1.7140898 \times 10^{-13}) = 12.765966 = \mathbf{12.77}$$



$$x = [PH_3] = [BCl_3]$$

$$K_c = [PH_3][BCl_3] = (x)(x) = x^2 = [8.4 \times 10^{-3}/3.0 L]^2 = 7.84 \times 10^{-6} = \mathbf{7.8 \times 10^{-6}}$$

b)



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

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

Temporarily assume $i = 1$.

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

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

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 M				x		x
Change	-x				+x		+x
Equilibrium	1.000 - x				x		x

The total concentration of all species is:

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

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

$$x = 0.037634 M$$

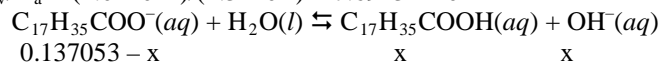
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

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

18.171 Molarity = $\left(\frac{0.42 \text{ g } C_{17}H_{35}COONa}{10.0 \text{ mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol } C_{17}H_{35}COONa}{306.45 \text{ g } C_{17}H_{35}COONa}\right)\left(\frac{1 \text{ mol } C_{17}H_{35}COO^-}{1 \text{ mol } C_{17}H_{35}COONa}\right)$

$$= 0.137053 M C_{17}H_{35}COO^-$$

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



$$K_b = 7.69231 \times 10^{-10} = \frac{[C_{17}H_{35}COOH][OH^-]}{[C_{17}H_{35}COO^-]}$$

$$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.137053 - x)} \quad \text{Assume } x \text{ is small compared to } 0.137053.$$

$$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.137053)}$$

$$x = 1.026769 \times 10^{-5} = [\text{OH}^-]$$

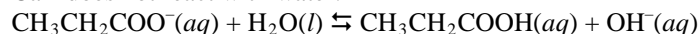
Check assumption: $[1.026768 \times 10^{-5} / 0.137053] \times 100\% = 0.007\%$, therefore the assumption is good.

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.026768 \times 10^{-5}) = 9.739298 \times 10^{-10} \text{ M } \text{H}_3\text{O}^+$$

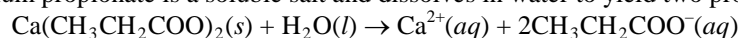
$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.739298 \times 10^{-10}) = 9.01147 = \mathbf{9.01}$$

- 18.172 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.



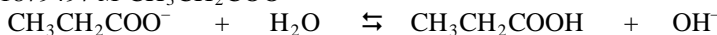
- b) Calcium propionate is a soluble salt and dissolves in water to yield two propionate ions:



The molarity of the solution is:

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

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



Initial	0.1879497 M	0	0
---------	-------------	---	---

Change	-x	+x	+x
--------	----	----	----

Equilibrium	0.1879497 - x	x	x
-------------	---------------	---	---

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

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

$$K_b = 7.69231 \times 10^{-10} = \frac{(x)(x)}{(0.1879497 - x)} \quad \text{Assume } x \text{ is small compared to } 0.1879497.$$

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

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

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

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.202401 \times 10^{-5}) = 8.31669 \times 10^{-10} \text{ M } \text{H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.31669 \times 10^{-10}) = 9.0800 = \mathbf{9.08}$$

- 18.173 a) Annual depositions:

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

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

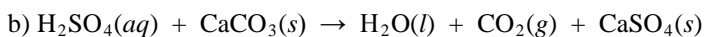
$$\text{H}_2\text{SO}_4: \left(\frac{1.0 \text{ H}_2\text{SO}_4}{9.5 \text{ total}} \right) (2.688 \text{ g/m}^2) = 0.282947 = 0.28 \text{ g/m}^2$$

$(\text{NH}_4)_2\text{SO}_4$ is a weak acid; NH_4HSO_4 has half the acidity per mole as H_2SO_4 so the equivalent amount of sulfuric acid deposition would be:

$$\left(\frac{1.56 \text{ g NH}_4\text{HSO}_4}{\text{m}^2} \right) \left(\frac{0.50 \text{ M NH}_4\text{HSO}_4}{1 \text{ M H}_2\text{SO}_4} \right) \left(\frac{98.08 \text{ g H}_2\text{SO}_4}{115.11 \text{ g NH}_4\text{HSO}_4} \right) = 0.664602 \text{ g/m}^2$$

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

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



There is a 1:1 mole ratio between H_2SO_4 and CaCO_3 .

Mass (lb) of CaCO_3 =

$$\left(9.4 \times 10^3 \text{ kg H}_2\text{SO}_4\right)\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)\left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.08 \text{ g H}_2\text{SO}_4}\right)\left(\frac{1 \text{ mol CaCO}_3}{1 \text{ mol H}_2\text{SO}_4}\right)\left(\frac{100.1 \text{ g CaCO}_3}{1 \text{ mol CaCO}_3}\right)\left(\frac{2.205 \text{ lb}}{1000 \text{ g}}\right) \\ = 2.1154 \times 10^4 = \mathbf{2.1 \times 10^4 \text{ lb CaCO}_3}$$

$$\text{c) Moles of H}^+ = \left(9.4 \times 10^3 \text{ kg H}_2\text{SO}_4\right)\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)\left(\frac{1 \text{ mol H}_2\text{SO}_4}{98.08 \text{ g H}_2\text{SO}_4}\right)\left(\frac{2 \text{ mol H}^+}{1 \text{ mol H}_2\text{SO}_4}\right) = 1.91680 \times 10^5 \text{ mol H}^+$$

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

$$\text{Molarity of H}^+ = \frac{1.91680 \times 10^5 \text{ mol H}^+}{3.0 \times 10^{10} \text{ L}} = 6.3893 \times 10^{-6} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (6.3893 \times 10^{-6}) = 5.1945 = \mathbf{5.19}$$

18.174 a) 0°C $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 1.139 \times 10^{-15}$
 $x = [\text{H}_3\text{O}^+] = 3.374907 \times 10^{-8} = \mathbf{3.375 \times 10^{-8} \text{ M H}_3\text{O}^+}$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.374907 \times 10^{-8}) = 7.471738 = \mathbf{7.4717}$
 50°C $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 5.474 \times 10^{-14}$
 $x = [\text{H}_3\text{O}^+] = 2.339658 \times 10^{-7} = \mathbf{2.340 \times 10^{-7} \text{ M H}_3\text{O}^+}$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.339658 \times 10^{-7}) = 6.6308476 = \mathbf{6.6308}$

b) 0°C $K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 3.64 \times 10^{-16}$
 $x = [\text{D}_3\text{O}^+] = 1.907878 \times 10^{-8} = \mathbf{1.91 \times 10^{-8} \text{ M D}_3\text{O}^+}$
 $\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (1.907878 \times 10^{-8}) = 7.719449 = \mathbf{7.719}$
 50°C $K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 7.89 \times 10^{-15}$
 $x = [\text{D}_3\text{O}^+] = 8.882567 \times 10^{-8} = \mathbf{8.88 \times 10^{-8} \text{ M D}_3\text{O}^+}$
 $\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (8.882567 \times 10^{-8}) = 7.0514615 = \mathbf{7.051}$

c) The deuterium atom has twice the mass of a normal hydrogen atom. The deuterium atom is held more strongly to the oxygen atom, so the degree of ionization is decreased.

$$18.175 \text{ Molarity of HX} = \left(\frac{12.0 \text{ g HX}}{\text{L}}\right)\left(\frac{1 \text{ mol HX}}{150. \text{ g HX}}\right) = 0.0800 \text{ M HX}$$

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

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

18.176 Acid HA: $\text{HA}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{A}^-(aq)$

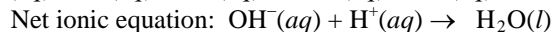
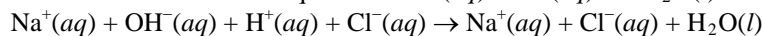
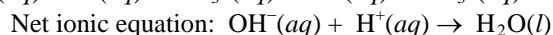
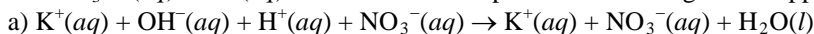
$$K_a = \frac{\left[\frac{0.010 \text{ mol}}{0.50 \text{ L}}\right]\left[\frac{0.010 \text{ mol}}{0.50 \text{ L}}\right]}{\left[\frac{0.050 \text{ mol}}{0.50 \text{ L}}\right]} = \mathbf{4.0 \times 10^{-3}}$$

Acid HB: $\text{HB}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{B}^-(aq)$

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

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

18.177 Treat $\text{H}_3\text{O}^+(aq)$ as $\text{H}^+(aq)$ because this corresponds to the listing in the Appendix.



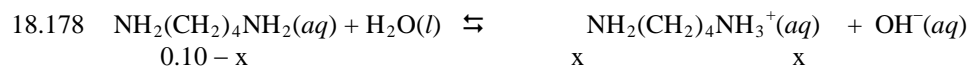
$$\Delta H_{\text{rxn}}^{\circ} = \sum[\Delta H_{\text{f}}^{\circ}(\text{products})] - \sum[\Delta H_{\text{f}}^{\circ}(\text{reactants})]$$

$$\Delta H_{\text{rxn}}^{\circ} = \{1 \Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}(l)]\} - \{1 \Delta H_{\text{f}}^{\circ}[\text{H}^+(aq)] + 1 \Delta H_{\text{f}}^{\circ}[\text{OH}^-(aq)]\}$$

$$\Delta H_{\text{rxn}}^{\circ} = [(1 \text{ mol})(-285.840 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (1 \text{ mol})(-229.94 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}}^{\circ} = -55.90 \text{ kJ}$$

b) The neutralization reaction of a strong acid and a strong base is essentially the reaction between $\text{H}^+(aq)$ and $\text{OH}^-(aq)$ to form $\text{H}_2\text{O}(l)$. Therefore, $\Delta H_{\text{rxn}}^{\circ}$ for KOH and HCl would be expected to be **-55.90 kJ**.



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

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

18.179 a) There are 20 OH^- ions for every 2 H_3O^+ ions; in other words, $[\text{OH}^-] = 10 \times [\text{H}_3\text{O}^+]$

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

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

$$[\text{H}_3\text{O}^+] = 3.162278 \times 10^{-8} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.162278 \times 10^{-8}) = 7.4999999 = \mathbf{7.5}$$

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

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

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

The H_3O^+ concentration is one million times greater than that of OH^- . You would have to draw one million H_3O^+ ions for every one OH^- .

18.180 a) As the pH of a water solution containing casein increases, the H^+ ions from the carboxyl groups on casein will be removed. This will increase the number of charged groups, and the solubility of the casein will increase.

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

18.181 Plan: Use Le Chatelier's principle.

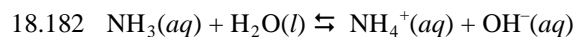
Solution:

a) The concentration of oxygen is higher in the lungs so the equilibrium shifts to the right.

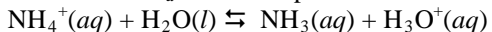
b) In an oxygen deficient environment, the equilibrium would shift to the left to release oxygen.

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 .



Convert to a K_a relationship:



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

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

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

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

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

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

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

c) Increasing the pH shifts the equilibria towards NH_3 . Ammonia is able to escape the solution as a gas.

18.183 Plan: The molarity 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 molarity of the solution. The total concentration of all species at equilibrium equals the apparent molarity 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 molarity of the solution (before acid dissociation).

$$M = \left(\frac{7.500 \text{ g CH}_3\text{CH}_2\text{COOH}}{100.0 \text{ mL solution}} \right) \left(\frac{1 \text{ mL}}{10^{-3} \text{ L}} \right) \left(\frac{1 \text{ mol CH}_3\text{CH}_2\text{COOH}}{74.08 \text{ g CH}_3\text{CH}_2\text{COOH}} \right) = 1.012419 = \mathbf{1.012 \text{ M CH}_3\text{CH}_2\text{COOH}}$$

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 $i = 1$.

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

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

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 M 0 0
<u>Change</u>	<u>-x +x +x</u>
Equilibrium	1.012419 - x x x

The total concentration of all species is:

$$\begin{aligned} [\text{CH}_3\text{CH}_2\text{COOH}] + [\text{H}_3\text{O}^+] + [\text{CH}_3\text{CH}_2\text{COO}^-] &= 1.016129032 \text{ M} \\ [1.012419 - x] + [x] + [x] &= 1.012419 + x = 1.016129032 \text{ M} \\ x &= 0.00371003 = \mathbf{0.004 \text{ M CH}_3\text{CH}_2\text{COO}^-} \end{aligned}$$

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

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

18.184 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

find

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 the pH.

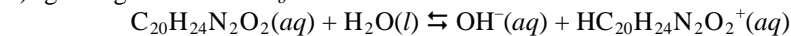
Solution:

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 :



Initial	$1.6 \times 10^{-3} \text{ M}$	0	0
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<u>Change</u>	$-x$	$+x$	$+x$
---------------	------	------	------

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

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

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

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

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

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.

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

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

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

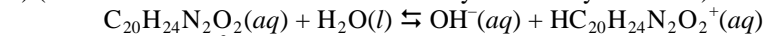
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.08834 \times 10^{-4}} = 9.18830513 \times 10^{-11} \text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (9.18830513 \times 10^{-11}) = 10.03676 = \mathbf{10.0}$$

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



Initial	$1.6 \times 10^{-3} \text{ M}$	0	0
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<u>Change</u>	$-x$	$+x$	$+x$
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Equilibrium	$1.6 \times 10^{-3} - x$	x	x
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$$K_b = 1.995262 \times 10^{-10} = \frac{[\text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+][\text{OH}^-]}{[\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2]}$$

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

Assume x is small compared to 1.6×10^{-3} .

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

$$x = 5.65015 \times 10^{-7} \text{ M OH}^-$$

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).

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

Initial	0.33 M	0	0
Change	-x	+x	+x
Equilibrium	0.33 - x	x	x

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

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

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

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

$$[\text{H}_3\text{O}^+] = x = 2.038252 \times 10^{-5} \text{ M}$$

Check assumption that x is small compared to 0.33:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.038252 \times 10^{-5}) = 4.69074 = \mathbf{4.7}$$

d) Quinine hydrochloride will be indicated as QHCl.

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

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

Initial	0.041566 M	0	0
Change	-x	+x	+x
Equilibrium	0.041566 - x	x	x

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

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

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

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

Check assumption that x is small compared to 0.33:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.233857 \times 10^{-6}) = 5.1406 = \mathbf{5.1}$$

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

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

$$\frac{[\text{HClO}]}{[\text{HClO}] + [\text{ClO}^-]} = \frac{1.0 \times 10^{-7}}{1.0 \times 10^{-7} + 2.9 \times 10^{-8}} = 0.775194 = \mathbf{0.78}$$

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

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

$$\frac{[\text{HClO}]}{[\text{HClO}] + [\text{ClO}^-]} = \frac{1.0 \times 10^{-10}}{1.0 \times 10^{-10} + 2.9 \times 10^{-8}} = 0.003436 = \mathbf{0.0034}$$

18.186 a) All scenes indicate equal initial amounts of each acid. The more H_3O^+ present, the stronger the acid is (greater K_a).

Increasing K_a : **HX < HZ < HY**

b) The $\text{p}K_a$ values increase in order of decreasing K_a values.

Increasing $\text{p}K_a$: **HY < HZ < HX**

c) The order of $\text{p}K_b$ is always the reverse of $\text{p}K_a$ values:

Increasing $\text{p}K_b$: **HX < HZ < HY**

d) Percent dissociation = $(2/8) \times 100\% = \mathbf{25\%}$

e) **NaY**, the weakest base, will give the highest pOH and the lowest pH.