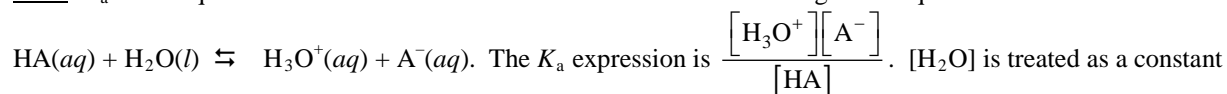


CHAPTER 18 ACID-BASE EQUILIBRIA

END-OF-CHAPTER PROBLEMS

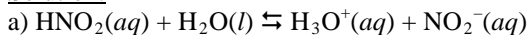
- 18.1 The Arrhenius definition classifies substances as being acids or bases by their behavior in the solvent water.
- 18.2 All Arrhenius acids contain hydrogen and produce hydronium ion (H_3O^+) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous 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 $\text{NH}_3(g)$ and $\text{HCl}(g)$ 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 (b) H_2O is a very weak Arrhenius base.

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

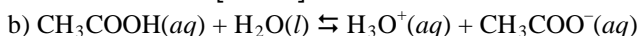


and omitted from the expression. Write the acid-dissociation reaction for each acid, following the generic equation, and then write the K_a expression.

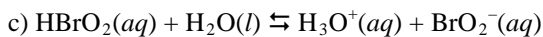
Solution:



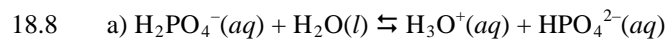
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$



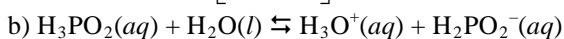
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$



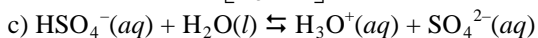
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{BrO}_2^-]}{[\text{HBrO}_2]}$$



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



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



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

18.9 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:



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

18.11 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.

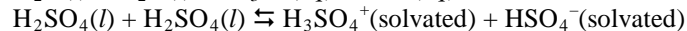
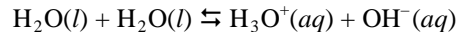
b) Strontium hydroxide, $\text{Sr}(\text{OH})_2$, is a **strong base**. Soluble compounds containing OH^- ions are strong bases. Sr is a Group 2 metal.

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.

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

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



18.14 a) pH increases by a value of 1.

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

- 18.15 Plan: The lower the concentration of hydronium (H_3O^+) ions, the higher the pH. pH increases as K_a or the molarity of acid decreases. Recall that $\text{p}K_a = -\log K_a$.
Solution:
 a) At equal concentrations, the acid with the larger K_a will ionize to produce more hydronium ions than the acid with the smaller K_a . The solution of an **acid with the smaller $K_a = 4 \times 10^{-5}$** has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 b) $\text{p}K_a$ is equal to $-\log K_a$. The smaller the K_a , the larger the $\text{p}K_a$ is. So the **acid with the larger $\text{p}K_a, 3.5$** , has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 c) **Lower concentration** of the same acid means lower concentration of hydronium ions produced. The 0.01 M solution has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 d) At the same concentration, strong acids dissociate to produce more hydronium ions than weak acids. The 0.1 M solution of a **weak acid** has a lower $[\text{H}_3\text{O}^+]$ and higher pH.
 e) Bases produce 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 $-\log [\text{OH}^-]$. At 25°C , the equilibrium constant for water ionization, K_w , equals 1×10^{-14} so $14 = \text{pH} + \text{pOH}$. As pOH decreases, pH increases. The solution of **$\text{pOH} = 6.0$** has the higher pH.

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

- 18.17 a) $\text{pH} = -\log (0.0333) = 1.47756 = \mathbf{1.478}$; **acidic**
 b) $\text{pOH} = -\log (0.0347) = 1.45967 = \mathbf{1.460}$; **basic**

- 18.18 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:

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

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

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

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

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

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

- 18.19 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 $14 = \text{pH} + \text{pOH}$.

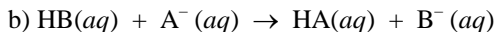
Solution:

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

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

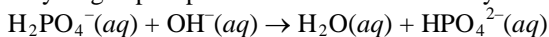
$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.23} = 5.8884 \times 10^{-10} = \mathbf{5.9 \times 10^{-10} \text{ M OH}^-}$$

- b) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.65 = \mathbf{8.35}$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.35} = 4.46684 \times 10^{-9} = \mathbf{4.5 \times 10^{-9} \text{ M H}_3\text{O}^+}$
 $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.65} = 2.23872 \times 10^{-6} = \mathbf{2.2 \times 10^{-6} \text{ M OH}^-}$
- 18.20 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:
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.52} = 3.01995 \times 10^{-5} \text{ M H}_3\text{O}^+$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.25} = 5.623413 \times 10^{-6} \text{ M H}_3\text{O}^+$
 $3.01995 \times 10^{-5} \text{ M} - 5.623413 \times 10^{-6} \text{ M} = 2.4576 \times 10^{-5} \text{ M OH}^-$ must be added.
Moles of $\text{OH}^- = \frac{2.4576 \times 10^{-5} \text{ mol}}{\text{L}} (5.6 \text{ L}) = 1.3763 \times 10^{-4} = \mathbf{1.4 \times 10^{-4} \text{ mol of OH}^-}$
- 18.21 The pH is decreasing so the solution is becoming more acidic. Therefore, H_3O^+ ion is added to decrease the pH.
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-8.92} = 1.20226 \times 10^{-9} \text{ M H}_3\text{O}^+$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.33} = 4.67735 \times 10^{-7} \text{ M H}_3\text{O}^+$
Add $(4.67735 \times 10^{-7} \text{ M} - 1.20226 \times 10^{-9} \text{ M})(87.5 \text{ mL})(10^{-3} \text{ L/1 mL})$
 $= 4.08216 \times 10^{-8} = \mathbf{4.1 \times 10^{-8} \text{ mol of H}_3\text{O}^+}$
- 18.22 Scene A has a pH of 4.8.
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.8} = 1.58489 \times 10^{-5} \text{ M H}_3\text{O}^+$
Scene B:
 $[\text{H}_3\text{O}^+] = (1.58489 \times 10^{-5} \text{ M H}_3\text{O}^+) \left(\frac{25 \text{ spheres}}{2 \text{ spheres}} \right) = 1.98 \times 10^{-4} \text{ M H}_3\text{O}^+$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log [1.98 \times 10^{-4}] = \mathbf{3.7}$
- 18.23 Water in its pure form has only a very small conductance. Its electrical conductivity is due mostly to dissolved ions.
- 18.24 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 .
b) $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-6.80} = 1.58489 \times 10^{-7} \text{ M H}_3\text{O}^+ = \mathbf{1.6 \times 10^{-7} \text{ M}}$ $[\text{H}_3\text{O}^+] = [\text{OH}^-]$
 $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1.58489 \times 10^{-7})(1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} = \mathbf{2.5 \times 10^{-14}}$
For a neutral solution: $\text{pH} = \mathbf{pOH} = \mathbf{6.80}$
- 18.25 The Brønsted-Lowry theory defines acids as proton donors and bases as proton acceptors, while the Arrhenius definition looks at acids as containing ionizable H atoms and at bases as containing hydroxide ions. In both definitions, an acid produces hydronium ions and a base produces hydroxide ions when added to water. Ammonia, 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.)
- 18.26 Every acid has a conjugate base, and every base has a conjugate acid. The acid has one more H and one more positive charge than the base from which it was formed.
- 18.27 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.

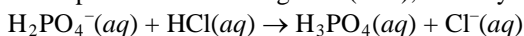


The spontaneous direction of a Brønsted-Lowry acid-base reaction is that the stronger acid will transfer a proton to the stronger base to produce the weaker acid and base. Thus at equilibrium there should be relatively more of weaker acid and base present than there will be of the stronger acid and base. 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.

- 18.28 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:



- 18.29 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.

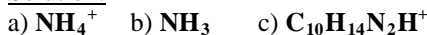
Solution:



- 18.30 a) PO₄³⁻ b) NH₃ c) S²⁻

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

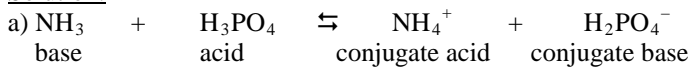
Solution:



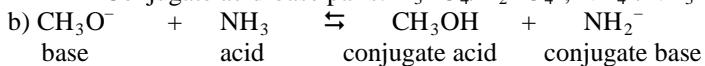
- 18.32 a) OH⁻ b) HSO₄⁻ c) H₃O⁺

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

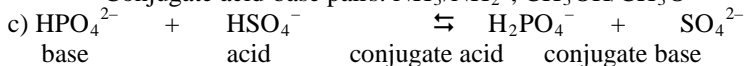
Solution:



Conjugate acid-base pairs: H₃PO₄/H₂PO₄⁻; NH₄⁺/NH₃



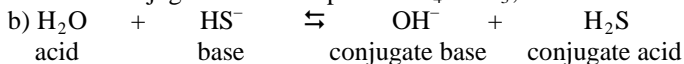
Conjugate acid-base pairs: NH₃/NH₂⁻; CH₃OH/CH₃O⁻



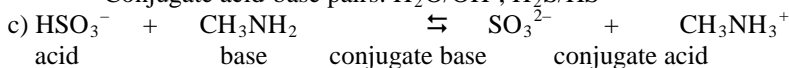
Conjugate acid-base pairs: HSO₄⁻/SO₄²⁻; H₂PO₄⁻/HPO₄²⁻

- 18.34 a) NH₄⁺ + CN⁻ ⇌ NH₃ + HCN
 acid base conjugate base conjugate acid

Conjugate acid-base pairs: NH₄⁺/NH₃; HCN/CN⁻



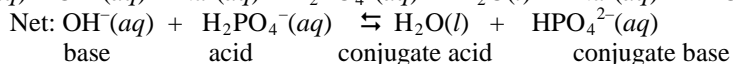
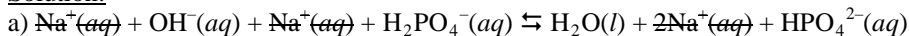
Conjugate acid-base pairs: H₂O/OH⁻; H₂S/HS⁻



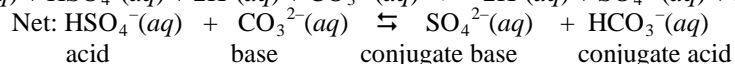
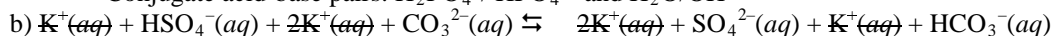
Conjugate acid-base pairs: HSO₃⁻/SO₃²⁻; CH₃NH₃⁺/CH₃NH₂

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

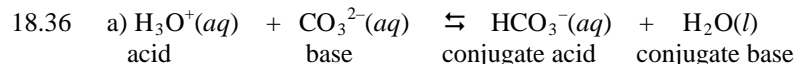
Solution:



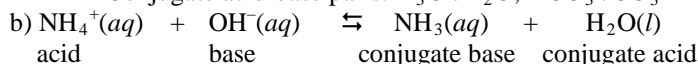
Conjugate acid-base pairs: $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and $\text{H}_2\text{O}/\text{OH}^-$



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



Conjugate acid-base pairs: $\text{H}_3\text{O}^+/\text{H}_2\text{O}$; $\text{HCO}_3^-/\text{CO}_3^{2-}$

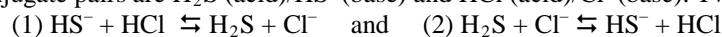


Conjugate acid-base pairs: $\text{NH}_4^+/\text{NH}_3$; $\text{H}_2\text{O}/\text{OH}^-$

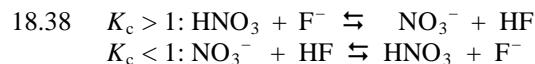
18.37 Plan: The two possible reactions involve reacting the acid from one conjugate pair with the base from the other conjugate pair. The reaction that favors the products ($K_c > 1$) is the one in which the stronger acid produces the weaker acid. The reaction that favors reactants ($K_c < 1$) is the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

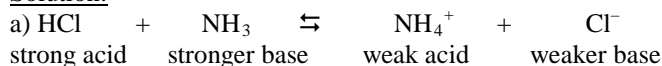


The first reaction is the reverse of the second. HCl is a strong acid and H_2S a weak acid. Reaction (1) with the stronger acid producing the weaker acid favors products and $K_c > 1$. Reaction (2) with the weaker acid forming the stronger acid favors the reactants and $K_c < 1$.

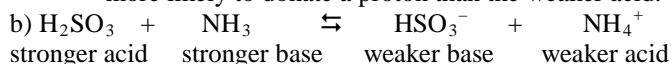


18.39 Plan: An acid-base reaction that favors the products ($K_c > 1$) is one in which the stronger acid produces the weaker acid. Use the figure to decide which of the two acids is the stronger acid.

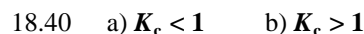
Solution:



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.

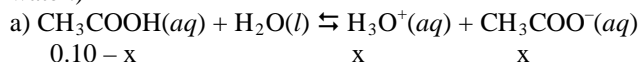


H_2SO_3 is ranked above NH_4^+ and is the stronger acid. NH_3 is a stronger base than HSO_3^- . The reaction proceeds toward the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $K_c > 1$.



- 18.41 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)

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



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

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

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

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

Since the H_3O^+ concentration from CH_3COOH is many times greater than that from H_2O , $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$.

b) The extremely low CH_3COOH concentration means the H_3O^+ concentration from CH_3COOH is near that from H_2O . Thus $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$.

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



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

$$x = [\text{H}_3\text{O}^+] = 1.8 \times 10^{-5}$$

$$[\text{CH}_3\text{COO}^-] = 0.1 + x = 0.1 \text{ M}$$

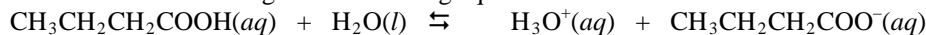
Thus, $[\text{CH}_3\text{COO}^-] > [\text{H}_3\text{O}^+]$

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

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

Solution:

Butanoic acid dissociates according to the following equation:



Initial:	0.15 M	0	0
Change:	-x	+x	+x

Equilibrium:	0.15 - x	x	x
--------------	----------	---	---

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

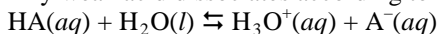
Thus, $[\text{H}_3\text{O}^+] = [\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-] = 1.51 \times 10^{-3} \text{ M}$

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

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

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

18.45 Any weak acid dissociates according to the following equation:



$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.88} = 1.31826 \times 10^{-5} \text{ M}$$

Thus, $[\text{H}_3\text{O}^+] = [\text{A}^-] = 1.31826 \times 10^{-5} \text{ M}$, and $[\text{HA}] = (0.035 - 1.31826 \times 10^{-5}) = 0.03499 \text{ M}$

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

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

- 18.46 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
<u>Change</u>	<u>—x</u>				<u>+x</u>		<u>+x</u>
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 $K_w = 1.0 \times 10^{-14}$

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

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

- 18.47 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
<u>Change</u>	<u>—x</u>				<u>+x</u>		<u>+x</u>
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.

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

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

- 18.48 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 ($[\text{H}_3\text{O}^+]$). K_a is found from the $\text{p}K_a$ by using the relationship $K_a = 10^{-\text{p}K_a}$.

Solution:

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

Concentration	$\text{ClCH}_2\text{COOH}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{ClCH}_2\text{COO}^-(aq)$		
Initial	1.25	0	0
Change	-x	+x	+x
Equilibrium	$1.25 - x$	x	x

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

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

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

$$x = 0.04106337$$

Check assumption that x is small compared to 1.25:

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

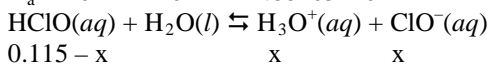
$$[\text{H}_3\text{O}^+] = [\text{ClCH}_2\text{COO}^-] = \mathbf{0.041 M}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (0.04106337) = 1.3865 = \mathbf{1.39}$$

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

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



$$0.115 - x$$

$$x$$

$$x$$

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

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

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

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

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

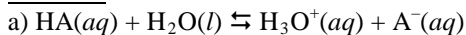
$$[\text{H}_3\text{O}^+] = [\text{ClO}^-] = \mathbf{5.8 \times 10^{-5} M}$$

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.75902 \times 10^{-5}) = 4.2397 = \mathbf{4.24}$$

- 18.50 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 is the concentration of the dissociated acid and $[\text{H}_3\text{O}^+]$. pH and $[\text{OH}^-]$ are determined from $[\text{H}_3\text{O}^+]$. Substitute $[\text{HA}]$, $[\text{A}^-]$, and $[\text{H}_3\text{O}^+]$ into the expression for K_a to find the value of K_a .

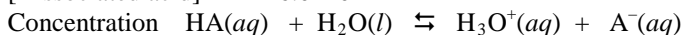
Solution:

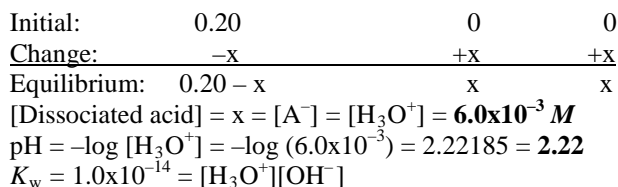


$$\text{Percent HA} = \frac{\text{dissociated acid}}{\text{initial acid}}(100)$$

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

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





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

pOH = -log [OH⁻] = -log (1.6666667x10⁻¹²) = 11.7782 = **11.78**

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

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

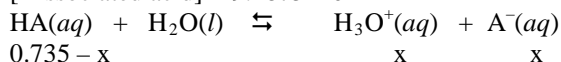
18.51 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of A⁻ and H₃O⁺. Then, pH and [OH⁻] are determined from [H₃O⁺].

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

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

[Dissociated acid] = 9.1875x10⁻² M



0.735 - x

x

x

[Dissociated acid] = x = [H₃O⁺] = **9.19x10⁻² M**

pH = -log [H₃O⁺] = -log (9.1875x10⁻²) = 1.03680 = **1.037**

[OH⁻] = K_w/[H₃O⁺] = (1.0x10⁻¹⁴)/(9.1875x10⁻²) = 1.0884x10⁻¹³ = **1.1x10⁻¹³ M**

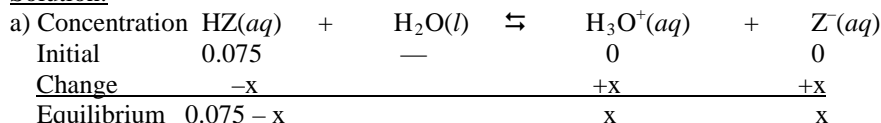
pOH = -log [OH⁻] = -log (1.0884x10⁻¹³) = 12.963197 = **12.963**

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

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

18.52 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 [H₃O⁺]. Use the expression for K_a to solve for x ([H₃O⁺]). OH⁻ and then pOH can be found from [H₃O⁺].

Solution:



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

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

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

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

[H₃O⁺] = x = 4.3732x10⁻³

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 × 10⁻⁴ c = -1.9125 × 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	HZ(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	Z ⁻ (aq)
Initial	0.045		—		0		0
Change	-x				+x		+x
Equilibrium	0.045 - x				x		x

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

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

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

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

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

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 b = 2.55 × 10⁻⁴ c = -1.1475 × 10⁻⁵

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

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

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

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

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

18.53 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	HQ(aq)	+	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	Q ⁻ (aq)
Initial	0.035		—		0		0
Change	-x				+x		+x
Equilibrium	0.035 - x				x		x

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

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

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

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

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

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.)

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

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

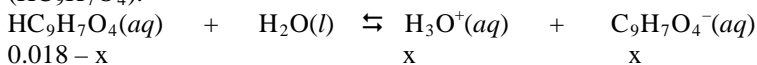
$$K_a = 1.28825 \times 10^{-5} = \frac{(x)(x)}{(0.65)}$$

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

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

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

18.54 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of aspirin (HC₉H₇O₄).



$$0.018 - x$$

$$x$$

$$x$$

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

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

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

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

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.

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

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

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

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

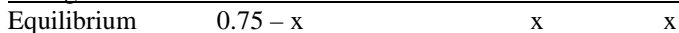
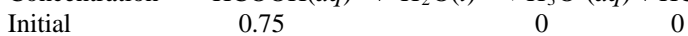
$$x = \frac{-3.6 \times 10^{-4} \pm \sqrt{(3.6 \times 10^{-4})^2 - 4(1)(-6.48 \times 10^{-6})}}{2(1)}$$

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

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

- 18.55 **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:



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

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

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

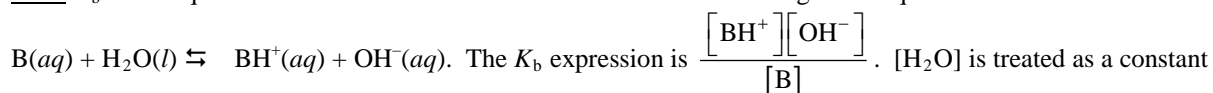
$$x = 1.161895 \times 10^{-2}$$

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

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

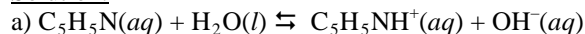
- 18.56 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an H^+ and allows the base to act as a proton-acceptor.
- 18.57 The negative charge and lone pair of the anion in many cases is able to extract a proton from water forming OH^- ions. Non-basic anions are from strong acids and include I^- , NO_3^- , Cl^- , ClO_4^- .
- 18.58 a) The species present are: **$\text{CH}_3\text{COOH}(aq)$, $\text{CH}_3\text{COO}^-(aq)$, $\text{H}_3\text{O}^+(aq)$, and $\text{OH}^-(aq)$.**
 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 H_3O^+ 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.

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

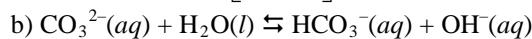


and omitted from the expression. Write the base-dissociation reaction for each base, showing the base accepting a proton from water, and then write the K_b expression.

Solution:

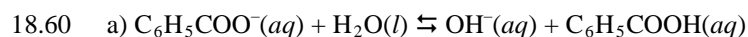


$$K_b = \frac{[C_5H_5NH^+][OH^-]}{[C_5H_5N]}$$

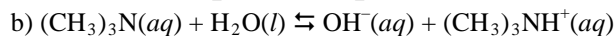


$$K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

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



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

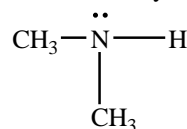


$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]}$$

18.61 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 $[OH^-]$. Use the expression for K_b to solve for x , $[OH^-]$, and then calculate $[H_3O^+]$ and pH.

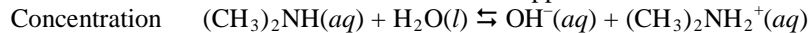
Solution:

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



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

The value for the dissociation constant is from Appendix C.



Initial 0.070 0 0

Change -x +x +x

Equilibrium 0.070 - x x x

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

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

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

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

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.

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

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

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

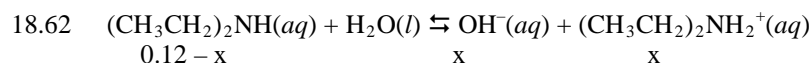
$$a = 1 \quad b = 5.9 \times 10^{-4} \quad c = -4.13 \times 10^{-5}$$

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

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

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

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



$$0.12 - x$$

$$x$$

$$x$$

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

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

Assume x 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.

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

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

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

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

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

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

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

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

18.63 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^- .

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

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

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

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

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

- 18.64 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 $pK_b = -\log K_b$.

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

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

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

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

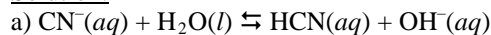
$$pK_a = -\log(1.17647 \times 10^{-8}) = 7.9294 = \mathbf{7.93}$$

- 18.65 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

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

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

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

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

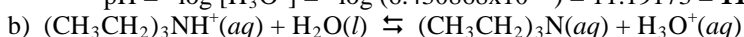
$$x = 1.555 \times 10^{-3} \text{ M } \text{OH}^-$$

Check assumption that x is small compared to 0.150:

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

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

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



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

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

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

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

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

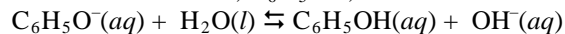
$$[\text{H}_3\text{O}^+] = x = 2.7735 \times 10^{-6} \text{ M}$$

Check assumption that x is small compared to 0.40:

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

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

- 18.66 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

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

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

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

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

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

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

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.1622776 \times 10^{-12}) = \mathbf{11.50}$$

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

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

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

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

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

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

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

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

- 18.67 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:

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

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

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

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

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

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

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

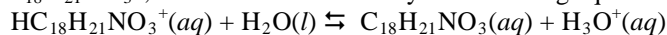
Check assumption that x is small compared to 0.873186:

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

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

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

18.68 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

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

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

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

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

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

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

Check assumption: $(1.7761737 \times 10^{-5}/0.050) \times 100\% = 0.04\%$ error, so the assumption is valid.

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

- 18.69 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^+ .
- 18.70 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.
- 18.71 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.
- 18.72 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.
- 18.73 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) HBrO_2 , bromous acid, is a stronger acid than HBrO , hypobromous acid, because there are more oxygen atoms in HBrO_2 than in HBrO .

18.74 a) **HBr** b) **H₃AsO₄** c) **HNO₂**

18.75 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, CuBr_2 , contains Cu^{2+} ion with $K_a = 3 \times 10^{-8}$. Aluminum bromide, AlBr_3 , contains Al^{3+} ion with $K_a = 1 \times 10^{-5}$. The concentrations of Cu^{2+} and Al^{3+} are equal, but the K_a of AlBr_3 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, ZnCl_2 , contains the Zn^{2+} ion with $K_a = 1 \times 10^{-9}$. Tin(II) chloride, SnCl_2 , contains the Sn^{2+} 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.

18.76 a) **FeCl₃** b) **BeCl₂**

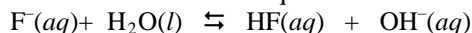
18.77 Salts that contain anions of weak acids and cations of strong bases are basic. Salts that contain cations of weak bases or small, highly charged metal cations, and anions of strong acids are acidic. Salts that contain cations of strong bases and anions of strong acids are neutral.

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 .)

18.78 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:

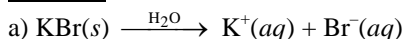


Sodium chloride, NaCl, is the salt of a strong base, NaOH, and strong acid, HCl. This combination yields a salt that is neutral in aqueous solution as neither Na^+ or Cl^- react in water to change the $[\text{H}_3\text{O}^+]$.

18.79 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 (CH_3COOH) is 1.8×10^{-5} , and the K_b for the conjugate base (NH_3) is 1.76×10^{-5} .

18.80 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.

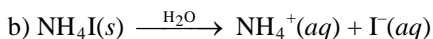
Solution:



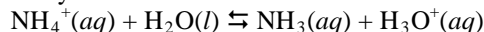
K^+ is the conjugate acid of a strong base, so it does not influence pH.

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.

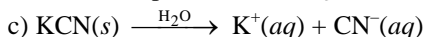


NH_4^+ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H_3O^+ as represented by the acid-dissociation reaction:



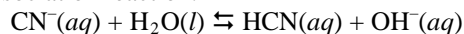
I^- is the conjugate base of a strong acid, so it will not influence the pH.

The production of H_3O^+ from the ammonium ion makes the solution of NH_4I **acidic**.



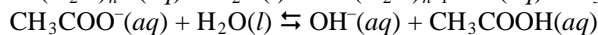
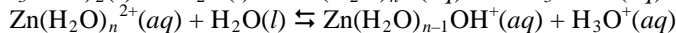
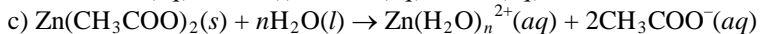
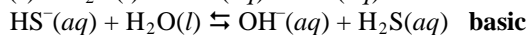
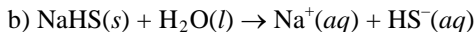
K^+ is the conjugate acid of a strong base, so it does not influence pH.

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**.

18.81 a) $\text{Cr}(\text{NO}_3)_3(s) + n\text{H}_2\text{O}(l) \rightarrow \text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + 3\text{NO}_3^-(aq)$
 $\text{Cr}(\text{H}_2\text{O})_n^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cr}(\text{H}_2\text{O})_{n-1}\text{OH}^{2+}(aq) + \text{H}_3\text{O}^+(aq)$ **acidic**



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

$K_b(\text{CH}_3\text{COO}^-) = K_w/K_a = (1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.5556 \times 10^{-10}$

The two K values are similar, so the solution is close to **neutral or slightly acidic**.

- 18.82 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)

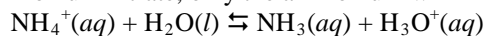
Iron(II) nitrate, $\text{Fe}(\text{NO}_3)_2$, is an acidic solution because the iron ion is a small, highly charged metal ion that acts as a weak acid and nitrate ion is the conjugate base of a strong acid, so it does not influence pH.

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: **$\text{NaHSO}_4 < \text{NH}_4\text{NO}_3 < \text{NaHCO}_3 < \text{Na}_2\text{CO}_3$**

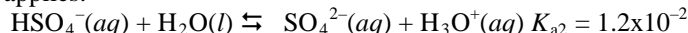
In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:



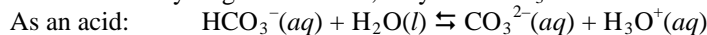
with $K_a = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

Therefore, the solution of ammonium nitrate is acidic.

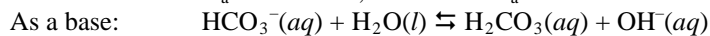
In solutions of sodium hydrogen sulfate, only HSO_4^- will influence pH. The hydrogen sulfate ion is amphoteric so both the acid and base dissociations must be evaluated for influence on pH. As a base, HSO_4^- is the conjugate base of a strong acid, so it will not influence pH. As an acid, HSO_4^- is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



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



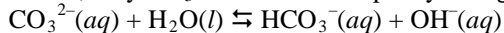
$K_a = 4.7 \times 10^{-11}$, the second K_a for carbonic acid



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

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

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



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

Therefore, the solution of sodium carbonate is basic.

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

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

- 18.83 a) **$\text{KClO}_2 > \text{MgCl}_2 > \text{FeCl}_2 > \text{FeCl}_3$**
 b) **$\text{NaBrO}_2 > \text{NaClO}_2 > \text{NaBr} > \text{NH}_4\text{Br}$**

- 18.84 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.
- 18.85 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.
- 18.86 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, water molecules solvate metal ions very well:

$$\text{Zn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Zn}(\text{H}_2\text{O})_4^{2+}(\text{aq})$$
 Water is a very weak Brønsted-Lowry base, but forms the Zn complex fairly well and is a reasonably strong Lewis base.
 b) The **cyanide ion** has a lone pair to donate from either the C or the N, and donates an electron pair to the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex. It is the Lewis base for the forward direction of this reaction. In the reverse direction, **water** donates one of the electron pairs on the oxygen to the $\text{Cu}(\text{CN})_4^{2-}$ and is the Lewis base.
 c) Because $K_c > 1$, the reaction proceeds in the direction written (left to right) and is driven by the stronger Lewis base, the **cyanide ion**.
- 18.87 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.
- 18.88 a) NH_3 can only act as a Brønsted-Lowry or Lewis base.
 b) AlCl_3 can only act as a Lewis acid.
- 18.89 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.
- 18.90 a) **Lewis acid** b) **Lewis base** c) **Lewis base** d) **Lewis acid**
- 18.91 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.

$$\text{Na}^+ + 6\text{H}_2\text{O} \rightleftharpoons \text{Na}(\text{H}_2\text{O})_6^+$$
 Lewis acid Lewis base adduct
 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.

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$$
 Lewis acid Lewis base adduct
 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.

$$\text{F}^- + \text{BF}_3 \rightleftharpoons \text{BF}_4^-$$
 Lewis base Lewis acid adduct
- 18.92 a) $\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}_3\text{O}^+$
 Lewis acid Lewis base

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

$$x = 2.17991 \times 10^{-6}$$

Check assumption that x is small compared to 1.056×10^{-5} :

$$\frac{2.17991 \times 10^{-6}}{1.056 \times 10^{-5}}(100) = 21\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 1.056×10^{-5} , and it is necessary to use the quadratic equation.

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

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

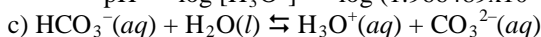
$$a = 1 \quad b = 4.5 \times 10^{-7} \quad c = -4.752 \times 10^{-12}$$

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

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

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

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



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

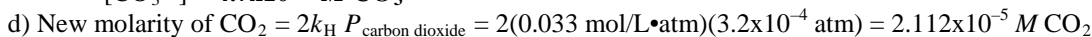
Use the unrounded x from part b).

$$K_{\text{overall}} = 4.7 \times 10^{-11} = \frac{[1.966489 \times 10^{-6} + x][x]}{[1.966489 \times 10^{-6} - x]}$$

Assume x is small compared to 2×10^{-6} .

$$K_{\text{overall}} = 4.7 \times 10^{-11} = \frac{[1.966489 \times 10^{-6}][x]}{[1.966489 \times 10^{-6}]}$$

$$[\text{CO}_3^{2-}] = \mathbf{4.7 \times 10^{-11} \text{ M } \text{CO}_3^{2-}}$$



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

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

Assume x is small compared to 2.112×10^{-5} .

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

$$x = 3.08286 \times 10^{-6}$$

Check assumption that x is small compared to 2.112×10^{-5} :

$$\frac{3.08286 \times 10^{-6}}{2.112 \times 10^{-5}}(100) = 15\% \text{ error, so the assumption is not valid.}$$

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 2.112×10^{-5} , and it is necessary to use the quadratic equation.

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

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

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

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

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

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

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

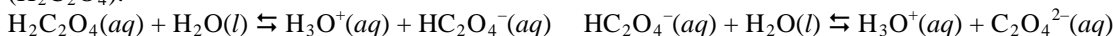
- 18.97 **Plan:** A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor. Recall that n is the main energy level and l is the orbital type.

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 $[\text{Kr}]5s^24d^{10}5p^2$. The four bonds to tin are formed by sp^3 hybrid orbitals, which completely fill the $5s$ and $5p$ orbitals. The $5d$ orbitals are empty and available for the bond with trimethylamine.

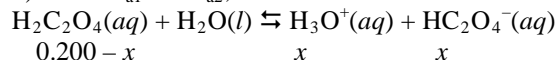
- 18.98 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$).



$$K_{a1} = 5.6 \times 10^{-2} = \frac{[\text{H}_3\text{O}^+][\text{HC}_2\text{O}_4^-]}{[\text{H}_2\text{C}_2\text{O}_4]} \quad K_{a2} = 5.4 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{O}_4^{2-}]}{[\text{HC}_2\text{O}_4^-]}$$

Assumption:

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



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

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

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

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

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

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

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

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

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

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

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

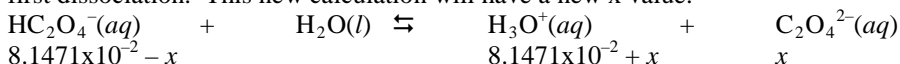
$$[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (8.1471 \times 10^{-2}) = 1.22743 \times 10^{-13} = \mathbf{1.2 \times 10^{-13} \text{ M}}$$

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

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

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

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



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

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

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

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

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

- 18.99 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 $[H_3O^+]$ 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: $[H_3O^+] = [HCl]$. The original solution pH:

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

Dilution 1: $M_1 V_1 = M_2 V_2$

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

$$[H_3O^+]_{HCl} = 1.0 \times 10^{-6} M H_3O^+$$

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

Dilution 2:

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

$$[H_3O^+]_{HCl} = 1.0 \times 10^{-7} M H_3O^+$$

Once the concentration of strong acid is close to the concentration of H_3O^+ from water autoionization, the $[H_3O^+]$ in the solution does not equal the initial concentration of the strong acid. The calculation of $[H_3O^+]$ must be based on the water ionization equilibrium:



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

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

$$K_w = [H_3O^+][OH^-] = (1 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

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

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

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

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

$$[H_3O^+] = (1.0 \times 10^{-7} + x) M = (1.0 \times 10^{-7} + 6.18034 \times 10^{-8}) M = 1.618034 \times 10^{-7} M H_3O^+$$

$$pH = -\log [H_3O^+] = -\log(1.618034 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$$

Dilution 3:

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

$$[H_3O^+]_{HCl} = 1.0 \times 10^{-8} M H_3O^+$$

The dilution gives an initial $[H_3O^+]$ of $1.0 \times 10^{-8} M$. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

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

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

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

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

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

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

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

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

Dilution 4:

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

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

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

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

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

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

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

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

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

$$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-9} + x) M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8}) M = 1.005012 \times 10^{-7} M \text{H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.005012 \times 10^{-7}) = 6.9978 = \mathbf{7.00}$$

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.

18.100 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:

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

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

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

Beaker B is not at equilibrium.

Concentrations in Beaker C:

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

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

$$Q = \frac{[\text{H}_3\text{O}^+][\text{Y}^-]}{[\text{HY}]} = \frac{[0.066667][0.066667]}{[0.133333]} = 0.0333345 = 0.033$$

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.

18.101 Compare the contribution of each acid by calculating the concentration of H_3O^+ produced by each.

For 3% hydrogen peroxide, first find initial molarity of H_2O_2 , assuming the density is 1.00 g/mL (the density of water).

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

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

	H_2O_2	+	H_2O	\rightleftharpoons	H_3O^+	+	HO_2^-
Initial	0.881834		—		0		0
Change	—x		—		+x		+x
Equilibrium	0.881834 — x		—		x		x

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

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

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

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

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

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

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

From Appendix C, K_a for phosphoric acid is 7.2×10^{-3} . The subsequent K_a values may be ignored. In this calculation x is not negligible since the initial concentration of acid is less than the K_a .

	H_3PO_4	+	H_2O	\rightleftharpoons	H_3O^+	+	H_2PO_4^-
Initial	1.0205×10^{-4}		—		0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	1.0205×10^{-4}		—		x		x

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

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

The problem will need to be solved as a quadratic.

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

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

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

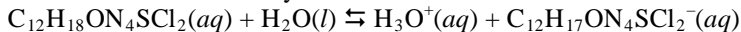
$$x = \frac{-7.2 \times 10^{-3} \pm \sqrt{(7.2 \times 10^{-3})^2 - 4(1)(-7.3476 \times 10^{-7})}}{2(1)}$$

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

The concentration of hydronium ion produced by the phosphoric acid, $1 \times 10^{-4} M$, is greater than the concentration produced by the hydrogen peroxide, $1 \times 10^{-6} M$. Therefore, the **phosphoric acid** contributes more H_3O^+ to the solution.

18.102 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.

18.103 M is the unknown molarity of the thiamine.



$$M - x \qquad \qquad \qquad x \qquad \qquad \qquad x$$

pH = 3.50

$$[\text{H}_3\text{O}^+] = 10^{-3.50} = 3.1623 \times 10^{-4} M = x$$

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

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

$$K_a = 3.37 \times 10^{-7} = \frac{(3.1623 \times 10^{-4})(3.1623 \times 10^{-4})}{(M - 3.1623 \times 10^{-4})}$$

$$M = 0.29705633 M$$

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

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

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

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

Assume x is small compared to 0.1879497.

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

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

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

$$[\text{H}_3\text{O}^+] = K_w / [\text{OH}^-] = (1.0 \times 10^{-14}) / (1.202401 \times 10^{-5}) = 8.31669 \times 10^{-10}\text{ M H}_3\text{O}^+$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (8.31669 \times 10^{-10}) = 9.0800 = \mathbf{9.08}$$

18.108 a) Annual depositions:

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

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

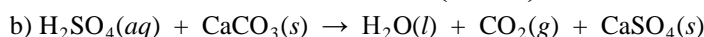
$$\text{H}_2\text{SO}_4: \left(\frac{1.0 \text{ H}_2\text{SO}_4}{9.5 \text{ total}} \right) (2.688 \text{ g/m}^2) = 0.282947 = 0.28 \text{ g/m}^2$$

$(\text{NH}_4)_2\text{SO}_4$ 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:

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

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

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



There is a 1:1 mole ratio between H_2SO_4 and CaCO_3 .

Mass (lb) of CaCO_3 =

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

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

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

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

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

- 18.109 a) 0°C $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 1.139 \times 10^{-15}$
 $x = [\text{H}_3\text{O}^+] = 3.374907 \times 10^{-8} = \mathbf{3.375 \times 10^{-8} M \text{H}_3\text{O}^+}$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.374907 \times 10^{-8}) = 7.471738 = \mathbf{7.4717}$
 50°C $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (x)(x) = 5.474 \times 10^{-14}$
 $x = [\text{H}_3\text{O}^+] = 2.339658 \times 10^{-7} = \mathbf{2.340 \times 10^{-7} M \text{H}_3\text{O}^+}$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.339658 \times 10^{-7}) = 6.6308476 = \mathbf{6.6308}$
b) 0°C $K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 3.64 \times 10^{-16}$
 $x = [\text{D}_3\text{O}^+] = 1.907878 \times 10^{-8} = \mathbf{1.91 \times 10^{-8} M \text{D}_3\text{O}^+}$
 $\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (1.907878 \times 10^{-8}) = 7.719449 = \mathbf{7.719}$
 50°C $K_w = [\text{D}_3\text{O}^+][\text{OD}^-] = (x)(x) = 7.89 \times 10^{-15}$
 $x = [\text{D}_3\text{O}^+] = 8.882567 \times 10^{-8} = \mathbf{8.88 \times 10^{-8} M \text{D}_3\text{O}^+}$
 $\text{pH} = -\log [\text{D}_3\text{O}^+] = -\log (8.882567 \times 10^{-8}) = 7.0514615 = \mathbf{7.051}$

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.

- 18.110 $\text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightleftharpoons [\text{H}_2\text{CO}_3(\text{aq})] + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_3^-(\text{aq})$
In an acidic solution (HCl), the equilibrium is shifted to the left, producing more gaseous CO_2 . In an alkaline solution (NaOH), the H_3O^+ formed is neutralized by the OH^- , shifting the equilibrium to the right and causing the solubility of CO_2 to increase.

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

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

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

18.112 Acid HA: $\text{HA}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$
 $K_a = \frac{[0.010 \text{ mol}/0.50 \text{ L}][0.010 \text{ mol}/0.50 \text{ L}]}{[0.050 \text{ mol}/0.50 \text{ L}]} = \mathbf{4.0 \times 10^{-3}}$

Acid HB: $\text{HB}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{B}^-(\text{aq})$
 $K_a = \frac{[0.010 \text{ mol}/0.25 \text{ L}][0.010 \text{ mol}/0.25 \text{ L}]}{[0.040 \text{ mol}/0.25 \text{ L}]} = \mathbf{1.0 \times 10^{-2}}$

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

- 18.113 a) There are 20 OH^- ions for every 2 H_3O^+ ions; in other words, $[\text{OH}^-] = 10 \times [\text{H}_3\text{O}^+]$

$K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+][\text{OH}^-]$
 $1.0 \times 10^{-14} = [\text{H}_3\text{O}^+](10)[\text{H}_3\text{O}^+]$
 $[\text{H}_3\text{O}^+] = 3.162278 \times 10^{-8} M$
 $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (3.162278 \times 10^{-8}) = 7.4999999 = \mathbf{7.5}$

b) For a pH of 4, $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4} = 1.0 \times 10^{-4} M$
 $[\text{OH}^-] = K_w/[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14})/(1.0 \times 10^{-4}) = 1.0 \times 10^{-10} M \text{OH}^-$
 $[\text{H}_3\text{O}^+]/[\text{OH}^-] = 1.0 \times 10^{-4}/1.0 \times 10^{-10} = 1.0 \times 10^6$

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^- .

- 18.114 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.

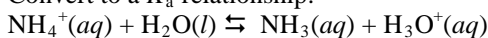
18.115 Plan: Use Le Chatelier's principle.

Solution:

- The concentration of oxygen is higher in the lungs so the equilibrium shifts to the **right**.
- In an oxygen deficient environment, the equilibrium would shift to the **left** to release oxygen.
- 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 .
- 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 .

18.116 $\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$

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

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

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

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

c) Increasing the pH shifts the equilibria towards NH_3 . Ammonia is able to escape the solution as a gas.

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

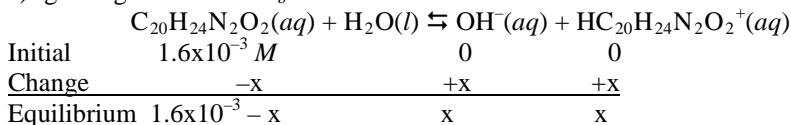
Solution:

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

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

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

a) Ignoring the smaller K_b :



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

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

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

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

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.

	$\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HC}_{20}\text{H}_{24}\text{N}_2\text{O}_2^+(aq)$		
Initial	$1.6 \times 10^{-3} \text{ M}$	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$1.6 \times 10^{-3} - x$	x	x

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

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

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:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (2.038252 \times 10^{-5}) = 4.69074 = \mathbf{4.7}$$

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:

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

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.233857 \times 10^{-6}) = 5.1406 = \mathbf{5.1}$$

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

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

$$\frac{[\text{HClO}]}{[\text{HClO}] + [\text{ClO}^-]} = \frac{2.9 \times 10^{-8}}{1.0 \times 10^{-7} + 2.9 \times 10^{-8}} = 0.224806 = \mathbf{0.22}$$

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

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

$$\frac{[\text{HClO}]}{[\text{HClO}] + [\text{ClO}^-]} = \frac{2.9 \times 10^{-8}}{1.0 \times 10^{-10} + 2.9 \times 10^{-8}} = 0.99656 = \mathbf{1.0}$$

18.119 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.