

CHAPTER 15

ACIDS AND BASES

15.3 Table 15.2 of the text contains a list of important Brønsted acids and bases. **(a)** both (why?), **(b)** base, **(c)** acid, **(d)** base, **(e)** acid, **(f)** base, **(g)** base, **(h)** base, **(i)** acid, **(j)** acid.

15.4 Recall that the conjugate base of a Brønsted acid is the species that remains when *one* proton has been removed from the acid.

- (a)** nitrite ion: NO_2^-
- (b)** hydrogen sulfate ion (also called bisulfate ion): HSO_4^-
- (c)** hydrogen sulfide ion (also called bisulfide ion): HS^-
- (d)** cyanide ion: CN^-
- (e)** formate ion: HCOO^-

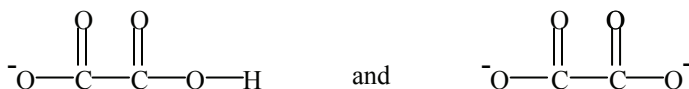
15.5 In general the components of the conjugate acid–base pair are on opposite sides of the reaction arrow. The base always has one fewer proton than the acid.

- (a)** The conjugate acid–base pairs are (1) HCN (acid) and CN^- (base) and (2) CH_3COO^- (base) and CH_3COOH (acid).
- (b)** (1) HCO_3^- (acid) and CO_3^{2-} (base) and (2) HCO_3^- (base) and H_2CO_3 (acid).
- (c)** (1) H_2PO_4^- (acid) and HPO_4^{2-} (base) and (2) NH_3 (base) and NH_4^+ (acid).
- (d)** (1) HClO (acid) and ClO^- (base) and (2) CH_3NH_2 (base) and CH_3NH_3^+ (acid).
- (e)** (1) H_2O (acid) and OH^- (base) and (2) CO_3^{2-} (base) and HCO_3^- (acid).

15.6 The conjugate acid of any base is just the base with a proton added.

- (a)** H_2S **(b)** H_2CO_3 **(c)** HCO_3^- **(d)** H_3PO_4 **(e)** H_2PO_4^-
- (f)** HPO_4^{2-} **(g)** H_2SO_4 **(h)** HSO_4^- **(i)** HSO_3^-

15.7 **(a)** The Lewis structures are



(b) H^+ and $\text{C}_2\text{H}_2\text{O}_4$ can act only as acids, C_2HO_4^- can act as both an acid and a base, and $\text{C}_2\text{O}_4^{2-}$ can act only as a base.

15.8 The conjugate base of any acid is simply the acid minus one proton.

- (a)** $\text{CH}_2\text{ClCOO}^-$ **(b)** IO_4^- **(c)** H_2PO_4^- **(d)** HPO_4^{2-} **(e)** PO_4^{3-}
- (f)** HSO_4^- **(g)** SO_4^{2-} **(h)** IO_3^- **(i)** SO_3^{2-} **(j)** NH_3
- (k)** HS^- **(l)** S^{2-} **(m)** OCl^-

$$15.15 \quad [\text{H}^+] = 1.4 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12} \text{ M}$$

$$15.16 \quad [\text{OH}^-] = 0.62 \text{ M}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.62} = 1.6 \times 10^{-14} \text{ M}$$

- 15.17 (a) HCl is a strong acid, so the concentration of hydrogen ion is also 0.0010 M. (What is the concentration of chloride ion?) We use the definition of pH.

$$\text{pH} = -\log[\text{H}^+] = -\log(0.0010) = 3.00$$

- (b) KOH is an ionic compound and completely dissociates into ions. We first find the concentration of hydrogen ion.

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.76} = 1.3 \times 10^{-14} \text{ M}$$

The pH is then found from its defining equation

$$\text{pH} = -\log[\text{H}^+] = -\log[1.3 \times 10^{-14}] = 13.89$$

- 15.18 (a) Ba(OH)₂ is ionic and fully ionized in water. The concentration of the hydroxide ion is $5.6 \times 10^{-4} \text{ M}$ (Why? What is the concentration of Ba²⁺?) We find the hydrogen ion concentration.

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-4}} = 1.8 \times 10^{-11} \text{ M}$$

The pH is then: $\text{pH} = -\log[\text{H}^+] = -\log(1.8 \times 10^{-11}) = 10.74$

- (b) Nitric acid is a strong acid, so the concentration of hydrogen ion is also $5.2 \times 10^{-4} \text{ M}$. The pH is:

$$\text{pH} = -\log[\text{H}^+] = -\log(5.2 \times 10^{-4}) = 3.28$$

- 15.19 Since $\text{pH} = -\log[\text{H}^+]$, we write $[\text{H}^+] = 10^{-\text{pH}}$

(a) $[\text{H}^+] = 10^{-2.42} = 3.8 \times 10^{-3} \text{ M}$

(c) $[\text{H}^+] = 10^{-6.96} = 1.1 \times 10^{-7} \text{ M}$

(b) $[\text{H}^+] = 10^{-11.21} = 6.2 \times 10^{-12} \text{ M}$

(d) $[\text{H}^+] = 10^{-15.00} = 1.0 \times 10^{-15} \text{ M}$

- 15.20 **Strategy:** Here we are given the pH of a solution and asked to calculate $[\text{H}^+]$. Because pH is defined as $\text{pH} = -\log[\text{H}^+]$, we can solve for $[\text{H}^+]$ by taking the antilog of the pH; that is, $[\text{H}^+] = 10^{-\text{pH}}$.

Solution: From Equation (15.4) of the text:

(a) $\text{pH} = -\log[\text{H}^+] = 5.20$

$$\log[\text{H}^+] = -5.20$$

To calculate $[\text{H}^+]$, we need to take the antilog of -5.20 .

$$[\text{H}^+] = 10^{-5.20} = 6.3 \times 10^{-6} \text{ M}$$

Check: Because the pH is between 5 and 6, we can expect $[\text{H}^+]$ to be between $1 \times 10^{-5} \text{ M}$ and $1 \times 10^{-6} \text{ M}$. Therefore, the answer is reasonable.

(b) $\text{pH} = -\log [\text{H}^+] = 16.00$

$$\log[\text{H}^+] = -16.00$$

$$[\text{H}^+] = 10^{-16.00} = 1.0 \times 10^{-16} \text{ M}$$

(c)

Strategy: We are given the concentration of OH^- ions and asked to calculate $[\text{H}^+]$. The relationship between $[\text{H}^+]$ and $[\text{OH}^-]$ in water or an aqueous solution is given by the ion-product of water, K_w [Equation (15.3) of the text].

Solution: The ion product of water is applicable to all aqueous solutions. At 25°C ,

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

Rearranging the equation to solve for $[\text{H}^+]$, we write

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{3.7 \times 10^{-9}} = 2.7 \times 10^{-6} \text{ M}$$

Check: Since the $[\text{OH}^-] < 1 \times 10^{-7} \text{ M}$ we expect the $[\text{H}^+]$ to be greater than $1 \times 10^{-7} \text{ M}$.

15.21

pH	$[\text{H}^+]$	Solution is:
< 7	$> 1.0 \times 10^{-7} \text{ M}$	acid
> 7	$< 1.0 \times 10^{-7} \text{ M}$	basic
$= 7$	$= 1.0 \times 10^{-7} \text{ M}$	neutral

15.22 (a) acidic (b) neutral (c) basic

15.23 The pH can be found by using Equation (15.8) of the text.

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.40 = 4.60$$

The hydrogen ion concentration can be found as in Example 15.4 of the text.

$$4.60 = -\log[\text{H}^+]$$

Taking the antilog of both sides:

$$[\text{H}^+] = 2.5 \times 10^{-5} \text{ M}$$

$$15.24 \quad 5.50 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.360 \text{ mol}}{1 \text{ L}} = 1.98 \times 10^{-3} \text{ mol KOH}$$

KOH is a strong base and therefore ionizes completely. The OH^- concentration equals the KOH concentration, because there is a 1:1 mole ratio between KOH and OH^- .

$$[\text{OH}^-] = 0.360 \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 0.444$$

15.25 We can calculate the OH^- concentration from the pOH.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.00 = 4.00$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 1.0 \times 10^{-4} \text{ M}$$

Since NaOH is a strong base, it ionizes completely. The OH^- concentration equals the initial concentration of NaOH.

$$[\text{NaOH}] = 1.0 \times 10^{-4} \text{ mol/L}$$

So, we need to prepare 546 mL of $1.0 \times 10^{-4} \text{ M}$ NaOH.

This is a dimensional analysis problem. We need to perform the following unit conversions.

$$\text{mol/L} \rightarrow \text{mol NaOH} \rightarrow \text{grams NaOH}$$

$$546 \text{ mL} = 0.546 \text{ L}$$

$$? \text{ g NaOH} = 546 \text{ mL} \times \frac{1.0 \times 10^{-4} \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{40.00 \text{ g NaOH}}{1 \text{ mol NaOH}} = 2.2 \times 10^{-3} \text{ g NaOH}$$

$$15.26 \quad \text{Molarity of the HCl solution is:} \quad \frac{18.4 \text{ g HCl} \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}}}{662 \times 10^{-3} \text{ L}} = 0.762 \text{ M}$$

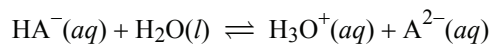
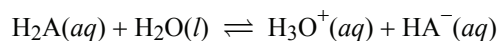
$$\text{pH} = -\log(0.762) = 0.118$$

15.31 A strong acid, such as HCl, will be completely ionized, choice (b).

A weak acid will only ionize to a lesser extent compared to a strong acid, choice (c).

A very weak acid will remain almost exclusively as the acid molecule in solution. Choice (d) is the best choice.

15.32 (1) The two steps in the ionization of a weak diprotic acid are:



The diagram that represents a weak diprotic acid is (c). In this diagram, we only see the first step of the ionization, because HA^- is a much weaker acid than H_2A .

(2) Both (b) and (d) are chemically implausible situations. Because HA^- is a much weaker acid than H_2A , you would not see a higher concentration of A^{2-} compared to HA^- .

15.33 (a) strong acid, (b) weak acid, (c) strong acid (first stage of ionization),
 (d) weak acid, (e) weak acid, (f) weak acid,
 (g) strong acid, (h) weak acid, (i) weak acid.

15.34 (a) strong base (b) weak base (c) weak base (d) weak base (e) strong base

15.35 The maximum possible concentration of hydrogen ion in a 0.10 M solution of HA is 0.10 M. This is the case if HA is a strong acid. If HA is a weak acid, the hydrogen ion concentration is less than 0.10 M. The pH corresponding to 0.10 M $[\text{H}^+]$ is 1.00. (Why three digits?) For a smaller $[\text{H}^+]$ the pH is larger than 1.00 (why?).

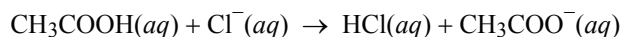
(a) false, the pH is greater than 1.00 (b) false, they are equal (c) true (d) false

15.36 (a) false, they are equal (b) true, find the value of $\log(1.00)$ on your calculator
 (c) true (d) false, if the acid is strong, $[\text{HA}] = 0.00 \text{ M}$

15.37 The direction should favor formation of $\text{F}^-(aq)$ and $\text{H}_2\text{O}(l)$. Hydroxide ion is a stronger base than fluoride ion, and hydrofluoric acid is a stronger acid than water.

15.38 Cl^- is the conjugate base of the strong acid, HCl. It is a negligibly weak base and has no affinity for protons. Therefore, the reaction will *not* proceed from left to right to any measurable extent.

Another way to think about this problem is to consider the possible products of the reaction.



The favored reaction is the one that proceeds from right to left. HCl is a strong acid and will ionize completely, donating all its protons to the base, CH_3COO^- .

15.43 We set up a table for the dissociation.

	$\text{C}_6\text{H}_5\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_6\text{H}_5\text{COO}^-(aq)$		
Initial (M):	0.10	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(0.10 - x)$	x	x

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

$$6.5 \times 10^{-5} = \frac{x^2}{(0.10 - x)}$$

$$x^2 + (6.5 \times 10^{-5})x - (6.5 \times 10^{-6}) = 0$$

Solving the quadratic equation:

$$x = 2.5 \times 10^{-3} M = [\text{H}^+]$$

$$\text{pH} = -\log(2.5 \times 10^{-3}) = \mathbf{2.60}$$

This problem could be solved more easily if we could assume that $(0.10 - x) \approx 0.10$. If the assumption is mathematically valid, then it would not be necessary to solve a quadratic equation, as we did above.

Re-solve the problem above, making the assumption. Was the assumption valid? What is our criterion for deciding?

- 15.44 Strategy:** Recall that a weak acid only partially ionizes in water. We are given the initial quantity of a weak acid (CH_3COOH) and asked to calculate the concentrations of H^+ , CH_3COO^- , and CH_3COOH at equilibrium. First, we need to calculate the initial concentration of CH_3COOH . In determining the H^+ concentration, we ignore the ionization of H_2O as a source of H^+ , so the major source of H^+ ions is the acid. We follow the procedure outlined in Section 15.5 of the text.

Solution:

Step 1: Calculate the concentration of acetic acid before ionization.

$$0.0560 \text{ g acetic acid} \times \frac{1 \text{ mol acetic acid}}{60.05 \text{ g acetic acid}} = 9.33 \times 10^{-4} \text{ mol acetic acid}$$

$$\frac{9.33 \times 10^{-4} \text{ mol}}{0.0500 \text{ L soln}} = 0.0187 M \text{ acetic acid}$$

Step 2: We ignore water's contribution to $[\text{H}^+]$. We consider CH_3COOH as the only source of H^+ ions.

Step 3: Letting x be the equilibrium concentration of H^+ and CH_3COO^- ions in mol/L, we summarize:

	$\text{CH}_3\text{COOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{CH}_3\text{COO}^-(aq)$
Initial (M):	0.0187		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.0187 - x$		x		x

Step 4: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x . You can look up the K_a value in Table 15.3 of the text.

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

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.0187 - x)}$$

At this point, we can make an assumption that x is very small compared to 0.0187. Hence,

$$0.0187 - x \approx 0.0187$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{0.0187}$$

$$x = \mathbf{5.8 \times 10^{-4} M} = [\text{H}^+] = [\text{CH}_3\text{COO}^-]$$

$$[\text{CH}_3\text{COOH}] = (0.0187 - 5.8 \times 10^{-4})M = \mathbf{0.0181 M}$$

Check: Testing the validity of the assumption,

$$\frac{5.8 \times 10^{-4}}{0.0187} \times 100\% = 3.1\% < 5\%$$

The assumption is valid.

15.45 First we find the hydrogen ion concentration.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-6.20} = 6.3 \times 10^{-7} M$$

If the concentration of $[\text{H}^+]$ is $6.3 \times 10^{-7} M$, that means that $6.3 \times 10^{-7} M$ of the weak acid, HA, ionized because of the 1:1 mole ratio between HA and H^+ . Setting up a table:

	$\text{HA}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{A}^-(aq)$
Initial (<i>M</i>):	0.010		0		0
Change (<i>M</i>):	-6.3×10^{-7}		$+6.3 \times 10^{-7}$		$+6.3 \times 10^{-7}$
Equilibrium (<i>M</i>):	≈ 0.010		6.3×10^{-7}		6.3×10^{-7}

Substituting into the acid ionization constant expression:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(6.3 \times 10^{-7})(6.3 \times 10^{-7})}{0.010} = 4.0 \times 10^{-11}$$

We have omitted the contribution to $[\text{H}^+]$ due to water.

15.46 A pH of 3.26 corresponds to a $[\text{H}^+]$ of $5.5 \times 10^{-4} M$. Let the original concentration of formic acid be *I*. If the concentration of $[\text{H}^+]$ is $5.5 \times 10^{-4} M$, that means that $5.5 \times 10^{-4} M$ of HCOOH ionized because of the 1:1 mole ratio between HCOOH and H^+ .

	$\text{HCOOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{HCOO}^-(aq)$
Initial (<i>M</i>):	<i>I</i>		0		0
Change (<i>M</i>):	-5.5×10^{-4}		$+5.5 \times 10^{-4}$		$+5.5 \times 10^{-4}$
Equilibrium (<i>M</i>):	$I - (5.5 \times 10^{-4})$		5.5×10^{-4}		5.5×10^{-4}

Substitute K_a and the equilibrium concentrations into the ionization constant expression to solve for *I*.

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

$$1.7 \times 10^{-4} = \frac{(5.5 \times 10^{-4})^2}{x - (5.5 \times 10^{-4})}$$

$$I = [\text{HCOOH}] = 2.3 \times 10^{-3} M$$

15.47 (a) Set up a table showing initial and equilibrium concentrations.

	$\text{C}_6\text{H}_5\text{COOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{C}_6\text{H}_5\text{COO}^-(aq)$
Initial (<i>M</i>):	0.20		0.00		0.00
Change (<i>M</i>):	$-x$		$+x$		$+x$
Equilibrium (<i>M</i>):	$(0.20 - x)$		x		x

Using the value of K_a from Table 15.3 of the text:

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

$$6.5 \times 10^{-5} = \frac{x^2}{(0.20 - x)}$$

We assume that x is small so $(0.20 - x) \approx 0.20$

$$6.5 \times 10^{-5} = \frac{x^2}{0.20}$$

$$x = 3.6 \times 10^{-3} M = [\text{H}^+] = [\text{C}_6\text{H}_5\text{COO}^-]$$

$$\text{Percent ionization} = \frac{3.6 \times 10^{-3} M}{0.20 M} \times 100\% = \mathbf{1.8\%}$$

(b) Set up a table as above.

	$\text{C}_6\text{H}_5\text{COOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{C}_6\text{H}_5\text{COO}^-(aq)$
Initial (M):	0.00020		0.00000		0.00000
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$(0.00020 - x)$		x		x

Using the value of K_a from Table 15.3 of the text:

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

$$6.5 \times 10^{-5} = \frac{x^2}{(0.00020 - x)}$$

In this case we cannot apply the approximation that $(0.00020 - x) \approx 0.00020$ (see the discussion in Example 15.8 of the text). We obtain the quadratic equation:

$$x^2 + (6.5 \times 10^{-5})x - (1.3 \times 10^{-8}) = 0$$

The positive root of the equation is $x = 8.6 \times 10^{-5} M$. (Is this less than 5% of the original concentration, $0.00020 M$? That is, is the acid more than 5% ionized?) The percent ionization is then:

$$\text{Percent ionization} = \frac{8.6 \times 10^{-5} M}{0.00020 M} \times 100\% = \mathbf{43\%}$$

Note that the extent to which a weak acid ionizes depends on the initial concentration of the acid. The more dilute the solution, the greater the percent ionization (see Figure 15.4 of the text).

15.48 Percent ionization is defined as:

$$\text{percent ionization} = \frac{\text{ionized acid concentration at equilibrium}}{\text{initial concentration of acid}} \times 100\%$$

For a monoprotic acid, HA, the concentration of acid that undergoes ionization is equal to the concentration of H^+ ions or the concentration of A^- ions at equilibrium. Thus, we can write:

$$\text{percent ionization} = \frac{[\text{H}^+]}{[\text{HA}]_0} \times 100\%$$

- (a) First, recognize that hydrofluoric acid is a weak acid. It is not one of the six strong acids, so it must be a weak acid.

Step 1: Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown x , that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of HF. From the stoichiometry of the reaction, it follows that the increase in concentration for both H^+ and F^- must be x . Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

	$\text{HF}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{F}^-(aq)$
Initial (M):	0.60		0		0
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$0.60 - x$		x		x

Step 2: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x .

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

You can look up the K_a value for hydrofluoric acid in Table 15.3 of your text.

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

At this point, we can make an assumption that x is very small compared to 0.60. Hence,

$$0.60 - x \approx 0.60$$

Oftentimes, assumptions such as these are valid if K is very small. A very small value of K means that a very small amount of reactants go to products. Hence, x is small. If we did not make this assumption, we would have to solve a quadratic equation.

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

Solving for x .

$$x = 0.021 \text{ M} = [\text{H}^+]$$

Step 3: Having solved for the $[\text{H}^+]$, calculate the percent ionization.

$$\begin{aligned} \text{percent ionization} &= \frac{[\text{H}^+]}{[\text{HF}]_0} \times 100\% \\ &= \frac{0.021 \text{ M}}{0.60 \text{ M}} \times 100\% = \mathbf{3.5\%} \end{aligned}$$

(b) – (c) are worked in a similar manner to part (a). However, as the initial concentration of HF becomes smaller, the assumption that x is very small compared to this concentration will no longer be valid. You must solve a quadratic equation.

$$\begin{aligned} \text{(b)} \quad K_a &= \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{(0.0046 - x)} = 7.1 \times 10^{-4} \\ x^2 + (7.1 \times 10^{-4})x - (3.3 \times 10^{-6}) &= 0 \\ x &= 1.5 \times 10^{-3} M \\ \text{Percent ionization} &= \frac{1.5 \times 10^{-3} M}{0.0046 M} \times 100\% = \mathbf{33\%} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad K_a &= \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{(0.00028 - x)} = 7.1 \times 10^{-4} \\ x^2 + (7.1 \times 10^{-4})x - (2.0 \times 10^{-7}) &= 0 \\ x &= 2.2 \times 10^{-4} M \\ \text{Percent ionization} &= \frac{2.2 \times 10^{-4} M}{0.00028 M} \times 100\% = \mathbf{79\%} \end{aligned}$$

As the solution becomes more dilute, the percent ionization increases.

15.49 Given 14% ionization, the concentrations must be:

$$\begin{aligned} [\text{H}^+] &= [\text{A}^-] = 0.14 \times 0.040 M = 0.0056 M \\ [\text{HA}] &= (0.040 - 0.0056) M = 0.034 M \end{aligned}$$

The value of K_a can be found by substitution.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.0056)^2}{0.034} = \mathbf{9.2 \times 10^{-4}}$$

15.50 The equilibrium is:

$$\text{C}_9\text{H}_8\text{O}_4(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_9\text{H}_7\text{O}_4^-(aq)$$

Initial (M):	0.20	0	0
Change (M):	- x	+ x	+ x
Equilibrium (M):	$0.20 - x$	x	x

$$\begin{aligned} \text{(a)} \quad K_a &= \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{C}_9\text{H}_8\text{O}_4]} \\ 3.0 \times 10^{-4} &= \frac{x^2}{(0.20 - x)} \end{aligned}$$

Assuming $(0.20 - x) \approx 0.20$

$$x = [\text{H}^+] = 7.7 \times 10^{-3} M$$

$$\text{Percent ionization} = \frac{x}{0.20} \times 100\% = \frac{7.7 \times 10^{-3} M}{0.20 M} \times 100\% = \mathbf{3.9\%}$$

- (b) At pH 1.00 the concentration of hydrogen ion is $0.10 M$ ($[\text{H}^+] = 10^{-\text{pH}}$). The extra hydrogen ions will tend to suppress the ionization of the weak acid (LeChâtelier's principle, Section 14.5 of the text). The position of equilibrium is shifted in the direction of the un-ionized acid. Let's set up a table of concentrations with the initial concentration of H^+ equal to $0.10 M$.

	$\text{C}_9\text{H}_8\text{O}_4(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_9\text{H}_7\text{O}_4^-(aq)$		
Initial (M):	0.20	0.10	0
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$0.20 - x$	$0.10 + x$	x

$$K_a = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{C}_9\text{H}_8\text{O}_4]}$$

$$3.0 \times 10^{-4} = \frac{x(0.10 + x)}{(0.20 - x)}$$

Assuming $(0.20 - x) \approx 0.20$ and $(0.10 + x) \approx 0.10$

$$x = 6.0 \times 10^{-4} M$$

$$\text{Percent ionization} = \frac{x}{0.20} \times 100\% = \frac{6.0 \times 10^{-4} M}{0.20 M} \times 100\% = \mathbf{0.30\%}$$

The high acidity of the gastric juices appears to enhance the rate of absorption of unionized aspirin molecules through the stomach lining. In some cases this can irritate these tissues and cause bleeding.

- 15.53 (a) We construct the usual table.

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$		
Initial (M):	0.10	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(0.10 - x)$	x	x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.10 - x)}$$

Assuming $(0.10 - x) \approx 0.10$, we have:

$$1.8 \times 10^{-5} = \frac{x^2}{0.10}$$

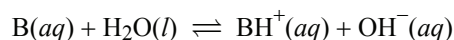
$$x = 1.3 \times 10^{-3} M = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.3 \times 10^{-3}) = 2.89$$

$$\text{pH} = 14.00 - 2.89 = \mathbf{11.11}$$

By following the identical procedure, we can show: **(b) pH = 8.96.**

15.54 Strategy: Weak bases only partially ionize in water.



Note that the concentration of the weak base given refers to the initial concentration before ionization has started. The pH of the solution, on the other hand, refers to the situation at equilibrium. To calculate K_b , we need to know the concentrations of all three species, [B], $[\text{BH}^+]$, and $[\text{OH}^-]$ at equilibrium. We ignore the ionization of water as a source of OH^- ions.

Solution: We proceed as follows.

Step 1: The major species in solution are B, OH^- , and the conjugate acid BH^+ .

Step 2: First, we need to calculate the hydroxide ion concentration from the pH value. Calculate the pOH from the pH. Then, calculate the OH^- concentration from the pOH.

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 10.66 = 3.34$$

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

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

Taking the antilog of both sides of the equation,

$$10^{-\text{pOH}} = [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-3.34} = 4.6 \times 10^{-4} M$$

Step 3: If the concentration of OH^- is $4.6 \times 10^{-4} M$ at equilibrium, that must mean that $4.6 \times 10^{-4} M$ of the base ionized. We summarize the changes.

	$\text{B}(aq)$	$+$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{BH}^+(aq)$	$+$	$\text{OH}^-(aq)$
Initial (M):	0.30				0		0
Change (M):	-4.6×10^{-4}				$+4.6 \times 10^{-4}$		$+4.6 \times 10^{-4}$
Equilibrium (M):	$0.30 - (4.6 \times 10^{-4})$				4.6×10^{-4}		4.6×10^{-4}

Step 4: Substitute the equilibrium concentrations into the ionization constant expression to solve for K_b .

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

$$K_b = \frac{(4.6 \times 10^{-4})^2}{(0.30)} = \mathbf{7.1 \times 10^{-7}}$$

- 15.55** A pH of 11.22 corresponds to a $[\text{H}^+]$ of $6.03 \times 10^{-12} \text{ M}$ and a $[\text{OH}^-]$ of $1.66 \times 10^{-3} \text{ M}$.

Setting up a table:

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$	
Initial (M):	1	0.00 0.00
Change (M):	-1.66×10^{-3}	$+1.66 \times 10^{-3}$ $+1.66 \times 10^{-3}$
Equilibrium (M):	$1 - (1.66 \times 10^{-3})$	1.66×10^{-3} 1.66×10^{-3}

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{(1.66 \times 10^{-3})(1.66 \times 10^{-3})}{1 - (1.66 \times 10^{-3})}$$

Assuming 1.66×10^{-3} is small relative to x , then

$$x = 0.15 \text{ M} = [\text{NH}_3]$$

- 15.56** The reaction is:

	$\text{NH}_3(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq)$
Initial (M):	0.080 0 0
Change (M):	$-x$ $+x$ $+x$
Equilibrium (M):	$0.080 - x$ x x

At equilibrium we have:

$$K_a = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{(0.080 - x)} \approx \frac{x^2}{0.080}$$

$$x = 1.2 \times 10^{-3} \text{ M}$$

$$\text{Percent NH}_3 \text{ present as NH}_4^+ = \frac{1.2 \times 10^{-3}}{0.080} \times 100\% = 1.5\%$$

- 15.61** If $K_{a_1} \gg K_{a_2}$, we can assume that the equilibrium concentration of hydrogen ion results only from the first stage of ionization. In the second stage this always leads to an expression of the type:

$$\frac{(c + y)(y)}{(c - y)} = K_{a_2}$$

where c represents the equilibrium hydrogen ion concentration found in the first stage. If $c \gg K_{a_2}$, we can assume $(c \pm y) \approx c$, and consequently $y = K_{a_2}$.

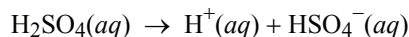
Is this conclusion also true for the second stage ionization of a triprotic acid like H_3PO_4 ?

15.62 The pH of a 0.040 M HCl solution (strong acid) is: $\text{pH} = -\log(0.040) = 1.40$. Follow the procedure for calculating the pH of a diprotic acid to calculate the pH of the sulfuric acid solution.

Strategy: Determining the pH of a diprotic acid in aqueous solution is more involved than for a monoprotic acid. The first stage of ionization for H_2SO_4 goes to completion. We follow the procedure for determining the pH of a strong acid for this stage. The conjugate base produced in the first ionization (HSO_4^-) is a weak acid. We follow the procedure for determining the pH of a weak acid for this stage.

Solution: We proceed according to the following steps.

Step 1: H_2SO_4 is a strong acid. The first ionization stage goes to completion. The ionization of H_2SO_4 is



The concentrations of all the species (H_2SO_4 , H^+ , and HSO_4^-) before and after ionization can be represented as follows.

	$\text{H}_2\text{SO}_4(aq)$	\rightarrow	$\text{H}^+(aq)$	$+$	$\text{HSO}_4^-(aq)$
Initial (M):	0.040		0		0
Change (M):	-0.040		+0.040		+0.040
Final (M):	0		0.040		0.040

Step 2: Now, consider the second stage of ionization. HSO_4^- is a weak acid. Set up a table showing the concentrations for the second ionization stage. Let x be the change in concentration. Note that the initial concentration of H^+ is 0.040 M from the first ionization.

	$\text{HSO}_4^-(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{SO}_4^{2-}(aq)$
Initial (M):	0.040		0.040		0
Change (M):	-x		+x		+x
Equilibrium (M):	$0.040 - x$		$0.040 + x$		x

Write the ionization constant expression for K_a . Then, solve for x . You can find the K_a value in Table 15.5 of the text.

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

$$1.3 \times 10^{-2} = \frac{(0.040 + x)(x)}{(0.040 - x)}$$

Since K_a is quite large, we cannot make the assumptions that

$$0.040 - x \approx 0.040 \quad \text{and} \quad 0.040 + x \approx 0.040$$

Therefore, we must solve a quadratic equation.

$$x^2 + 0.053x - (5.2 \times 10^{-4}) = 0$$

$$x = \frac{-0.053 \pm \sqrt{(0.053)^2 - 4(1)(-5.2 \times 10^{-4})}}{2(1)}$$

$$x = \frac{-0.053 \pm 0.070}{2}$$

$$x = 8.5 \times 10^{-3} M \quad \text{or} \quad x = -0.062 M$$

The second solution is physically impossible because you cannot have a negative concentration. The first solution is the correct answer.

Step 3: Having solved for x , we can calculate the H^+ concentration at equilibrium. We can then calculate the pH from the H^+ concentration.

$$[\text{H}^+] = 0.040 M + x = [0.040 + (8.5 \times 10^{-3})]M = 0.049 M$$

$$\text{pH} = -\log(0.049) = \mathbf{1.31}$$

Without doing any calculations, could you have known that the pH of the sulfuric acid would be lower (more acidic) than that of the hydrochloric acid?

- 15.63** There is no H_2SO_4 in the solution because HSO_4^- has no tendency to accept a proton to produce H_2SO_4 . (Why?) We are only concerned with the ionization:

	$\text{HSO}_4^-(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{SO}_4^{2-}(aq)$
Initial (M):	0.20		0.00		0.00
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	(0.20 - x)		$+x$		$+x$

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

$$1.3 \times 10^{-2} = \frac{(x)(x)}{(0.20 - x)}$$

Solving the quadratic equation:

$$x = [\text{H}^+] = [\text{SO}_4^{2-}] = \mathbf{0.045 M}$$

$$[\text{HSO}_4^-] = (0.20 - 0.045) M = \mathbf{0.16 M}$$

- 15.64** For the first stage of ionization:

	$\text{H}_2\text{CO}_3(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{HCO}_3^-(aq)$
Initial (M):	0.025		0.00		0.00
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	(0.025 - x)		x		x

$$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$4.2 \times 10^{-7} = \frac{x^2}{(0.025 - x)} \approx \frac{x^2}{0.025}$$

$$x = 1.0 \times 10^{-4} M$$

For the second ionization,

	$\text{HCO}_3^-(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{CO}_3^{2-}(aq)$
Initial (M):	1.0×10^{-4}		1.0×10^{-4}		0.00
Change (M):	$-x$		$+x$		$+x$
Equilibrium (M):	$(1.0 \times 10^{-4}) - x$		$(1.0 \times 10^{-4}) + x$		x

$$K_{a_2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

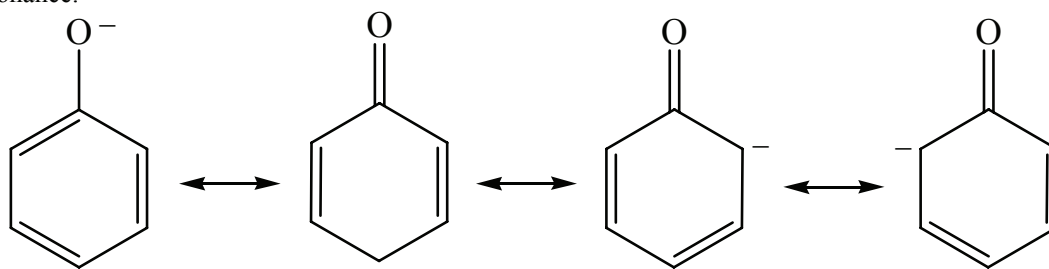
$$4.8 \times 10^{-11} = \frac{[(1.0 \times 10^{-4}) + x](x)}{(1.0 \times 10^{-4}) - x} \approx \frac{(1.0 \times 10^{-4})(x)}{(1.0 \times 10^{-4})}$$

$$x = 4.8 \times 10^{-11} \text{ M}$$

Since HCO_3^- is a very weak acid, there is little ionization at this stage. Therefore we have:

$$[\text{H}^+] = [\text{HCO}_3^-] = 1.0 \times 10^{-4} \text{ M} \text{ and } [\text{CO}_3^{2-}] = x = 4.8 \times 10^{-11} \text{ M}$$

- 15.67** The strength of the H–X bond is the dominant factor in determining the strengths of binary acids. As with the hydrogen halides (see Section 15.9 of the text), the H–X bond strength decreases going down the column in Group 6A. The compound with the weakest H–X bond will be the strongest binary acid: $\text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$.
- 15.68** All the listed pairs are oxoacids that contain different central atoms whose elements are in the same group of the periodic table and have the same oxidation number. In this situation the acid with the most electronegative central atom will be the strongest.
- (a) $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4$.
- (b) $\text{H}_3\text{PO}_4 > \text{H}_3\text{AsO}_4$
- 15.69** The CHCl_2COOH is a stronger acid than CH_2ClCOOH . Having two electronegative chlorine atoms compared to one, will draw more electron density toward itself, making the O–H bond more polar. The hydrogen atom in CHCl_2COOH is more easily ionized compared to the hydrogen atom in CH_2ClCOOH .
- 15.70** The conjugate bases are $\text{C}_6\text{H}_5\text{O}^-$ from phenol and CH_3O^- from methanol. The $\text{C}_6\text{H}_5\text{O}^-$ is stabilized by resonance:



The CH_3O^- ion has no such resonance stabilization. A more stable conjugate base means an increase in the strength of the acid.

- 15.75** (a) The K^+ cation does not hydrolyze. The Br^- anion is the conjugate base of the strong acid HBr. Therefore, Br^- will not hydrolyze either, and the solution is neutral, $pH \approx 7$.
- (b) Al^{3+} is a small metal cation with a high charge, which hydrolyzes to produce H^+ ions. The NO_3^- anion does not hydrolyze. It is the conjugate base of the strong acid, HNO_3 . The solution will be acidic, $pH < 7$.
- (c) The Ba^{2+} cation does not hydrolyze. The Cl^- anion is the conjugate base of the strong acid HCl. Therefore, Cl^- will not hydrolyze either, and the solution is neutral, $pH \approx 7$.
- (d) Bi^{3+} is a small metal cation with a high charge, which hydrolyzes to produce H^+ ions. The NO_3^- anion does not hydrolyze. It is the conjugate base of the strong acid, HNO_3 . The solution will be acidic, $pH < 7$.

15.76 Strategy: In deciding whether a salt will undergo hydrolysis, ask yourself the following questions: Is the cation a highly charged metal ion or an ammonium ion? Is the anion the conjugate base of a weak acid? If yes to either question, then hydrolysis will occur. In cases where both the cation and the anion react with water, the pH of the solution will depend on the relative magnitudes of K_a for the cation and K_b for the anion (see Table 15.7 of the text).

Solution: We first break up the salt into its cation and anion components and then examine the possible reaction of each ion with water.

- (a) The Na^+ cation does not hydrolyze. The Br^- anion is the conjugate base of the strong acid HBr. Therefore, Br^- will not hydrolyze either, and the solution is **neutral**.
- (b) The K^+ cation does not hydrolyze. The SO_3^{2-} anion is the conjugate base of the weak acid HSO_3^- and will hydrolyze to give HSO_3^- and OH^- . The solution will be **basic**.
- (c) Both the NH_4^+ and NO_2^- ions will hydrolyze. NH_4^+ is the conjugate acid of the weak base NH_3 , and NO_2^- is the conjugate base of the weak acid HNO_2 . From Tables 15.3 and 15.4 of the text, we see that the K_a of NH_4^+ (5.6×10^{-10}) is greater than the K_b of NO_2^- (2.2×10^{-11}). Therefore, the solution will be **acidic**.
- (d) Cr^{3+} is a small metal cation with a high charge, which hydrolyzes to produce H^+ ions. The NO_3^- anion does not hydrolyze. It is the conjugate base of the strong acid, HNO_3 . The solution will be **acidic**.
- 15.77** There are two possibilities: (i) MX is the salt of a strong acid and a strong base so that neither the cation nor the anion react with water to alter the pH and (ii) MX is the salt of a weak acid and a weak base with K_a for the acid equal to K_b for the base. The hydrolysis of one would be exactly offset by the hydrolysis of the other.
- 15.78** There is an inverse relationship between acid strength and conjugate base strength. As acid strength decreases, the proton accepting power of the conjugate base increases. In general the weaker the acid, the stronger the conjugate base. All three of the potassium salts ionize completely to form the conjugate base of the respective acid. The greater the pH, the stronger the conjugate base, and therefore, the weaker the acid.

The order of increasing acid strength is **HZ < HY < HX**.

- 15.79** The salt, sodium acetate, completely dissociates upon dissolution, producing 0.36 M $[\text{Na}^+]$ and 0.36 M $[\text{CH}_3\text{COO}^-]$ ions. The $[\text{CH}_3\text{COO}^-]$ ions will undergo hydrolysis because they are a weak base.

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

Initial (M):	0.36	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(0.36 - x)$	$+x$	$+x$

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

$$5.6 \times 10^{-10} = \frac{x^2}{(0.36 - x)}$$

Assuming $(0.36 - x) \approx 0.36$, then

$$x = [\text{OH}^-] = 1.4 \times 10^{-5}$$

$$\text{pOH} = -\log(1.4 \times 10^{-5}) = 4.85$$

$$\text{pH} = 14.00 - 4.85 = \mathbf{9.15}$$

- 15.80** The salt ammonium chloride completely ionizes upon dissolution, producing 0.42 M $[\text{NH}_4^+]$ and 0.42 M $[\text{Cl}^-]$ ions. NH_4^+ will undergo hydrolysis because it is a weak acid (NH_4^+ is the conjugate acid of the weak base, NH_3).

Step 1: Express the equilibrium concentrations of all species in terms of initial concentrations and a single unknown x , that represents the change in concentration. Let $(-x)$ be the depletion in concentration (mol/L) of NH_4^+ . From the stoichiometry of the reaction, it follows that the increase in concentration for both H_3O^+ and NH_3 must be x . Complete a table that lists the initial concentrations, the change in concentrations, and the equilibrium concentrations.

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

Initial (M):	0.42	0.00	0.00
Change (M):	$-x$	$+x$	$+x$
Equilibrium (M):	$(0.42 - x)$	x	x

Step 2: You can calculate the K_a value for NH_4^+ from the K_b value of NH_3 . The relationship is

$$K_a \times K_b = K_w$$

or

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

Step 3: Write the ionization constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant (K_a), solve for x .

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

$$5.6 \times 10^{-10} = \frac{x^2}{0.42 - x} \approx \frac{x^2}{0.42}$$

$$x = [\text{H}^+] = 1.5 \times 10^{-5} \text{ M}$$

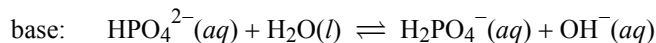
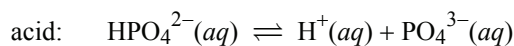
$$\text{pH} = -\log(1.5 \times 10^{-5}) = 4.82$$

Since NH_4Cl is the salt of a weak base (aqueous ammonia) and a strong acid (HCl), we expect the solution to be slightly acidic, which is confirmed by the calculation.



HCO_3^- has a greater tendency to hydrolyze than to ionize ($K_b > K_a$). The solution will be basic ($\text{pH} > 7$).

15.82 The acid and base reactions are:

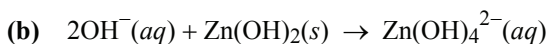


K_a for HPO_4^{2-} is 4.8×10^{-13} . Note that HPO_4^{2-} is the conjugate base of H_2PO_4^- , so K_b is 1.6×10^{-7} . Comparing the two K 's, we conclude that the monohydrogen phosphate ion is a much stronger proton acceptor (base) than a proton donor (acid). The solution will be **basic**.

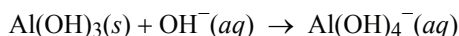
15.85 Metal ions with high oxidation numbers are unstable. Consequently, these metals tend to form covalent bonds (rather than ionic bonds) with oxygen. Covalent metal oxides are acidic while ionic metal oxides are basic. The latter oxides contain the O^{2-} ion which reacts with water as follows:



15.86 The most basic oxides occur with metal ions having the lowest positive charges (or lowest oxidation numbers).



15.88 $\text{Al}(\text{OH})_3$ is an amphoteric hydroxide. The reaction is:



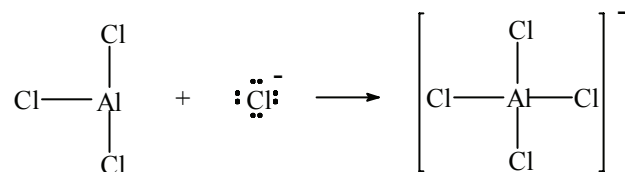
This is a Lewis acid-base reaction. Can you identify the acid and base?

15.91 (a) Lewis acid; see the reaction with water shown in Section 15.12 of the text.

(b) Lewis base; water combines with H^+ to form H_3O^+ .

- (c) Lewis base.
- (d) Lewis acid; SO_2 reacts with water to form H_2SO_3 . Compare to CO_2 above. Actually, SO_2 can also act as a Lewis base under some circumstances.
- (e) Lewis base; see the reaction with H^+ to form ammonium ion.
- (f) Lewis base; see the reaction with H^+ to form water.
- (g) Lewis acid; does H^+ have any electron pairs to donate?
- (h) Lewis acid; compare to the example of NH_3 reacting with BF_3 .

15.92 AlCl_3 is a Lewis acid with an incomplete octet of electrons and Cl^- is the Lewis base donating a pair of electrons.



- 15.93** (a) Both molecules have the same acceptor atom (boron) and both have exactly the same structure (trigonal planar). Fluorine is more electronegative than chlorine so we would predict based on electronegativity arguments that boron trifluoride would have a greater affinity for unshared electron pairs than boron trichloride.
- (b) Since it has the larger positive charge, iron(III) should be a stronger Lewis acid than iron(II).

15.94 By definition Brønsted acids are proton donors, therefore such compounds must contain at least one hydrogen atom. In Problem 15.91, Lewis acids that do not contain hydrogen, and therefore are not Brønsted acids, are CO_2 , SO_2 , and BCl_3 . Can you name others?

15.95 The ionization of any acid is an endothermic process. The higher the temperature, the greater the K_a value. Formic acid will be a stronger acid at 40°C than at 25°C .

15.96 We first find the number of moles of CO_2 produced in the reaction:

$$0.350 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol CO}_2}{1 \text{ mol NaHCO}_3} = 4.17 \times 10^{-3} \text{ mol CO}_2$$

$$V_{\text{CO}_2} = \frac{n_{\text{CO}_2} RT}{P} = \frac{(4.17 \times 10^{-3} \text{ mol})(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(37.0 + 273)\text{K}}{(1.00 \text{ atm})} = \mathbf{0.106 \text{ L}}$$

15.97 Choice (c) because 0.70 M KOH has a higher pH than 0.60 M NaOH . Adding an equal volume of 0.60 M NaOH lowers the $[\text{OH}^-]$ to 0.65 M , hence lowering the pH.

15.98 If we assume that the unknown monoprotic acid is a strong acid that is 100% ionized, then the $[\text{H}^+]$ concentration will be 0.0642 M .

$$\text{pH} = -\log(0.0642) = 1.19$$

Since the actual pH of the solution is higher, the acid must be a weak acid.

15.99 (a) For the forward reaction NH_4^+ and NH_3 are the conjugate acid and base pair, respectively. For the reverse reaction NH_3 and NH_2^- are the conjugate acid and base pair, respectively.

(b) H^+ corresponds to NH_4^+ ; OH^- corresponds to NH_2^- . For the neutral solution, $[\text{NH}_4^+] = [\text{NH}_2^-]$.

15.100 The reaction of a weak acid with a strong base is driven to completion by the formation of water. Irrespective of whether the strong base is reacting with a strong monoprotic acid or a weak monoprotic acid, the same number of moles of acid is required to react with a constant number of moles of base. Therefore the volume of base required to react with the same concentration of acid solutions (either both weak, both strong, or one strong and one weak) will be the same.

$$\mathbf{15.101} \quad K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{HA}] \approx 0.1 \text{ M}$$

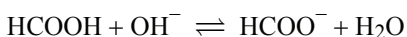
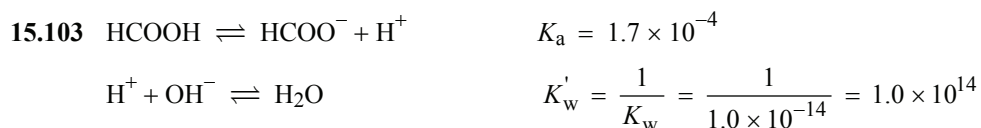
$$[\text{A}^-] \approx 0.1 \text{ M}$$

Therefore,

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

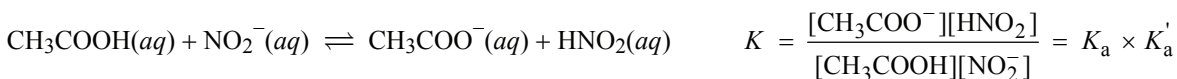
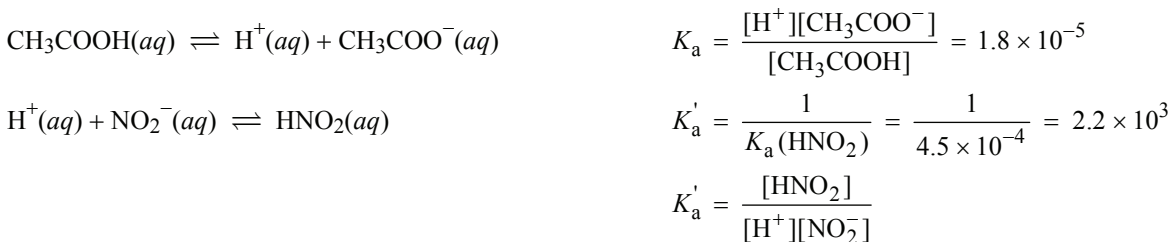
$$[\text{OH}^-] = \frac{K_w}{K_a}$$

15.102 High oxidation state leads to covalent compounds and low oxidation state leads to ionic compounds. Therefore, CrO is ionic and basic and CrO_3 is covalent and acidic.



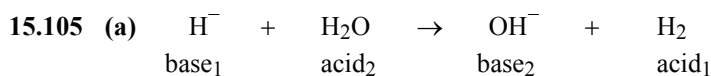
$$K = K_a K'_w = (1.7 \times 10^{-4})(1.0 \times 10^{14}) = \mathbf{1.7 \times 10^{10}}$$

15.104 We can write two equilibria that add up to the equilibrium in the problem.



The equilibrium constant for this sum is the product of the equilibrium constants of the component reactions.

$$K = K_a \times K'_a = (1.8 \times 10^{-5})(2.2 \times 10^3) = 4.0 \times 10^{-2}$$



(b) H^- is the reducing agent and H_2O is the oxidizing agent.

15.106 In this specific case the K_a of ammonium ion is the same as the K_b of acetate ion [$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10}$, $K_b(\text{CH}_3\text{COO}^-) = 5.6 \times 10^{-10}$]. The two are of exactly (to two significant figures) equal strength. The solution will have **pH 7.00**.

What would the pH be if the concentration were 0.1 M in ammonium acetate? 0.4 M?

15.107 $K_b = 8.91 \times 10^{-6}$

$$K_a = \frac{K_w}{K_b} = 1.1 \times 10^{-9}$$

$$\text{pH} = 7.40$$

$$[\text{H}^+] = 10^{-7.40} = 3.98 \times 10^{-8}$$

$$K_a = \frac{[\text{H}^+][\text{conjugate base}]}{[\text{acid}]}$$

Therefore,

$$\frac{[\text{conjugate base}]}{[\text{acid}]} = \frac{K_a}{[\text{H}^+]} = \frac{1.1 \times 10^{-9}}{3.98 \times 10^{-8}} = 0.028$$

15.108 The fact that fluorine attracts electrons in a molecule more strongly than hydrogen should cause NF_3 to be a poor electron pair donor and a poor base. **NH_3** is the stronger base.

15.109 Because the P–H bond is weaker, there is a greater tendency for PH_4^+ to ionize. Therefore, PH_3 is a weaker base than NH_3 .

15.110 The autoionization for deuterium-substituted water is: $\text{D}_2\text{O} \rightleftharpoons \text{D}^+ + \text{OD}^-$

$$[\text{D}^+][\text{OD}^-] = 1.35 \times 10^{-15} \quad (1)$$

(a) The definition of pD is: $\text{pD} = -\log[\text{D}^+] = -\log\sqrt{1.35 \times 10^{-15}} = 7.43$

(b) To be acidic, the **pD** must be **< 7.43**.

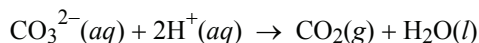
(c) Taking $-\log$ of both sides of equation (1) above:

$$-\log[D^+] + -\log[OD^-] = -\log(1.35 \times 10^{-15})$$

$$\mathbf{pD + pOD = 14.87}$$

- 15.111 (a) HNO_2 (b) HF (c) BF_3 (d) NH_3 (e) H_2SO_3
 (f) HCO_3^- and CO_3^{2-}

The reactions for (f) are: $\text{HCO}_3^-(aq) + \text{H}^+(aq) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$



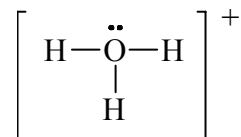
15.112 First we must calculate the molarity of the trifluoromethane sulfonic acid. (Molar mass = 150.1 g/mol)

$$\text{Molarity} = \frac{0.616 \text{ g} \times \frac{1 \text{ mol}}{150.1 \text{ g}}}{0.250 \text{ L}} = 0.0164 \text{ M}$$

Since trifluoromethane sulfonic acid is a strong acid and is 100% ionized, the $[\text{H}^+]$ is 0.0165 M.

$$\mathbf{pH = -\log(0.0164) = 1.79}$$

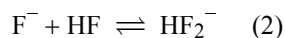
15.113 (a) The Lewis structure of H_3O^+ is:



Note that this structure is very similar to the Lewis structure of NH_3 . The geometry is **trigonal pyramidal**.

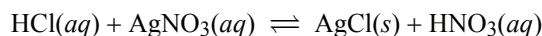
(b) H_4O^{2+} does *not* exist because the positively charged H_3O^+ has no affinity to accept the positive H^+ ion. If H_4O^{2+} existed, it would have a tetrahedral geometry.

15.114 The reactions are $\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$ (1)

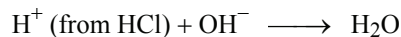


Note that for equation (2), the equilibrium constant is relatively large with a value of 5.2. This means that the equilibrium lies to the right. Applying Le Châtelier's principle, as HF ionizes in the first step, the F^- that is produced is partially removed in the second step. More HF must ionize to compensate for the removal of the F^- , at the same time producing more H^+ .

15.115 The equations are: $\text{Cl}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCl}(aq) + \text{HClO}(aq)$

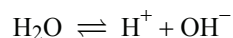
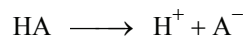


In the presence of OH^- ions, the first equation is shifted to the right:



Therefore, the concentration of HClO increases. (The ‘bleaching action’ is due to ClO^- ions.)

15.116 (a) We must consider both the complete ionization of the strong acid, and the partial ionization of water.



From the above two equations, the $[\text{H}^+]$ in solution is:

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad (1)$$

We can also write:

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

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

Substituting into Equation (1):

$$[\text{H}^+] = [\text{A}^-] + \frac{K_w}{[\text{H}^+]}$$

$$[\text{H}^+]^2 = [\text{A}^-][\text{H}^+] + K_w$$

$$[\text{H}^+]^2 - [\text{A}^-][\text{H}^+] - K_w = 0$$

Solving a quadratic equation:

$$[\text{H}^+] = \frac{[\text{A}^-] \pm \sqrt{[\text{A}^-]^2 + 4K_w}}{2}$$

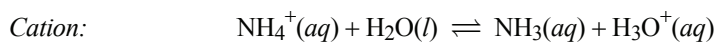
(b) For the strong acid, HCl, with a concentration of $1.0 \times 10^{-7} M$, the $[\text{Cl}^-]$ will also be $1.0 \times 10^{-7} M$.

$$[\text{H}^+] = \frac{[\text{Cl}^-] \pm \sqrt{[\text{Cl}^-]^2 + 4K_w}}{2} = \frac{1 \times 10^{-7} \pm \sqrt{(1 \times 10^{-7})^2 + 4(1 \times 10^{-14})}}{2}$$

$$[\text{H}^+] = 1.6 \times 10^{-7} M \text{ (or } -6.0 \times 10^{-8} M, \text{ which is impossible)}$$

$$\text{pH} = -\log[1.6 \times 10^{-7}] = \mathbf{6.80}$$

15.117 We examine the hydrolysis of the cation and anion separately.

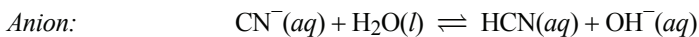


Initial (<i>M</i>):	2.00	0	0
Change (<i>M</i>):	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
Equilibrium (<i>M</i>):	2.00 - <i>x</i>	<i>x</i>	<i>x</i>

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

$$5.6 \times 10^{-10} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00}$$

$$x = 3.35 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$$



Initial (M):	2.00	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	2.00 - x	x	x

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$2.0 \times 10^{-5} = \frac{y^2}{2.00 - y} \approx \frac{y^2}{2.00}$$

$$y = 6.32 \times 10^{-3} \text{ M} = [\text{OH}^-]$$

CN^- is stronger as a base than NH_4^+ is as an acid. Some OH^- produced from the hydrolysis of CN^- will be neutralized by H_3O^+ produced from the hydrolysis of NH_4^+ .

	$\text{H}_3\text{O}^+(aq)$	+	$\text{OH}^-(aq)$	\rightarrow	$2\text{H}_2\text{O}(l)$
Initial (M):	3.35×10^{-5}		6.32×10^{-3}		
Change (M):	-3.35×10^{-5}		-3.35×10^{-5}		
Final (M):	0		6.29×10^{-3}		

$$[\text{OH}^-] = 6.29 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.20$$

$$\text{pH} = 11.80$$

15.118 The solution for the first step is standard:

	$\text{H}_3\text{PO}_4(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	+	$\text{H}_2\text{PO}_4^-(aq)$
Initial (M):	0.100		0.000		0.000
Change (M):	-x		+x		+x
Equil. (M):	$(0.100 - x)$		x		x

$$K_{a_1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

$$7.5 \times 10^{-3} = \frac{x^2}{(0.100 - x)}$$

In this case we probably cannot say that $(0.100 - x) \approx 0.100$ due to the magnitude of K_a . We obtain the quadratic equation:

$$x^2 + (7.5 \times 10^{-3})x - (7.5 \times 10^{-4}) = 0$$

The positive root is $x = 0.0239 M$. We have:

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 M$$

$$[\text{H}_3\text{PO}_4] = (0.100 - 0.0239) M = 0.076 M$$

For the second ionization:

	$\text{H}_2\text{PO}_4^-(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{HPO}_4^{2-}(aq)$
Initial (M):	0.0239		0.0239		0.000
Change (M):	-y		+y		+y
Equil (M):	$(0.0239 - y)$		$(0.0239 + y)$		y

$$K_{a_2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$6.2 \times 10^{-8} = \frac{(0.0239 + y)(y)}{(0.0239 - y)} \approx \frac{(0.0239)(y)}{(0.0239)}$$

$$y = 6.2 \times 10^{-8} M.$$

Thus,

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 M$$

$$[\text{HPO}_4^{2-}] = y = 6.2 \times 10^{-8} M$$

We set up the problem for the third ionization in the same manner.

	$\text{HPO}_4^{2-}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{PO}_4^{3-}(aq)$
Initial (M):	6.2×10^{-8}		0.0239		0
Change (M):	-z		+z		+z
Equil. (M):	$(6.2 \times 10^{-8}) - z$		$0.0239 + z$		z

$$K_{a_3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$4.8 \times 10^{-13} = \frac{(0.0239 + z)(z)}{(6.2 \times 10^{-8}) - z} \approx \frac{(0.239)(z)}{(6.2 \times 10^{-8})}$$

$$z = 1.2 \times 10^{-18} M$$

The equilibrium concentrations are:

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.0239 M$$

$$[\text{H}_3\text{PO}_4] = 0.076 M$$

$$[\text{HPO}_4^{2-}] = 6.2 \times 10^{-8} M$$

$$[\text{PO}_4^{3-}] = 1.2 \times 10^{-18} M$$

15.119 (a) We carry an additional significant figure throughout this calculation to minimize rounding errors.

$$\text{Number of moles NaOH} = M \times \text{vol (L)} = 0.0568 M \times 0.0138 \text{ L} = 7.838 \times 10^{-4} \text{ mol}$$

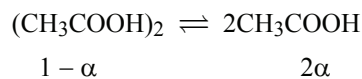
If the acid were all dimer, then:

$$\text{mol of dimer} = \frac{\text{mol NaOH}}{2} = \frac{7.838 \times 10^{-4} \text{ mol}}{2} = 3.919 \times 10^{-4} \text{ mol}$$

If the acetic acid were all dimer, the pressure that would be exerted would be:

$$P = \frac{nRT}{V} = \frac{(3.919 \times 10^{-4} \text{ mol})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(324 \text{ K})}{0.360 \text{ L}} = 0.02896 \text{ atm}$$

However, the actual pressure is 0.0342 atm. If α mol of dimer dissociates to monomers, then 2α monomer forms.



The total moles of acetic acid is:

$$\text{moles dimer} + \text{monomer} = (1 - \alpha) + 2\alpha = 1 + \alpha$$

Using partial pressures:

$$\begin{aligned} P_{\text{observed}} &= P(1 + \alpha) \\ 0.0342 \text{ atm} &= (0.02896 \text{ atm})(1 + \alpha) \\ \alpha &= \mathbf{0.181} \end{aligned}$$

(b) The equilibrium constant is:

$$K_p = \frac{P_{\text{CH}_3\text{COOH}}^2}{P_{(\text{CH}_3\text{COOH})_2}} = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2 (P_{\text{observed}})^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right) P_{\text{observed}}} = \frac{4\alpha^2 P_{\text{observed}}}{1 - \alpha^2} = \mathbf{4.63 \times 10^{-3}}$$

15.120 $0.100 M \text{Na}_2\text{CO}_3 \rightarrow 0.200 M \text{Na}^+ + 0.100 M \text{CO}_3^{2-}$

First stage:

	$\text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) + \text{OH}^-(\text{aq})$		
Initial (M):	0.100	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	0.100 - x	x	x

$$K_1 = \frac{K_w}{K_2} = \frac{1.0 \times 10^{-14}}{4.8 \times 10^{-11}} = 2.1 \times 10^{-4}$$

$$K_1 = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

$$2.1 \times 10^{-4} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = 4.6 \times 10^{-3} M = [\text{HCO}_3^-] = [\text{OH}^-]$$

Second stage:

	$\text{HCO}_3^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq) + \text{OH}^-(aq)$
Initial (M):	$4.6 \times 10^{-3} \qquad 0 \qquad 4.6 \times 10^{-3}$
Change (M):	$-y \qquad +y \qquad +y$
Equilibrium (M):	$(4.6 \times 10^{-3}) - y \qquad y \qquad (4.6 \times 10^{-3}) + y$

$$K_2 = \frac{[\text{H}_2\text{CO}_3][\text{OH}^-]}{[\text{HCO}_3^-]}$$

$$2.4 \times 10^{-8} = \frac{y[(4.6 \times 10^{-3}) + y]}{(4.6 \times 10^{-3}) - y} \approx \frac{(y)(4.6 \times 10^{-3})}{(4.6 \times 10^{-3})}$$

$$y = 2.4 \times 10^{-8} M$$

At equilibrium:

$$[\text{Na}^+] = 0.200 M$$

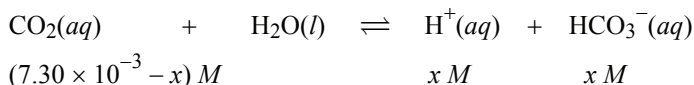
$$[\text{HCO}_3^-] = (4.6 \times 10^{-3}) M - (2.4 \times 10^{-8}) M \approx 4.6 \times 10^{-3} M$$

$$[\text{H}_2\text{CO}_3] = 2.4 \times 10^{-8} M$$

$$[\text{OH}^-] = (4.6 \times 10^{-3}) M + (2.4 \times 10^{-8}) M \approx 4.6 \times 10^{-3} M$$

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-3}} = 2.2 \times 10^{-12} M$$

15.121 $[\text{CO}_2] = kP = (2.28 \times 10^{-3} \text{ mol/L}\cdot\text{atm})(3.20 \text{ atm}) = 7.30 \times 10^{-3} M$



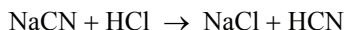
$$K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]}$$

$$4.2 \times 10^{-7} = \frac{x^2}{(7.30 \times 10^{-3}) - x} \approx \frac{x^2}{7.30 \times 10^{-3}}$$

$$x = 5.5 \times 10^{-5} M = [\text{H}^+]$$

pH = 4.26

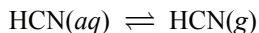
15.122 When NaCN is treated with HCl, the following reaction occurs.



HCN is a very weak acid, and only partially ionizes in solution.



The main species in solution is HCN which has a tendency to escape into the gas phase.



Since the HCN(g) that is produced is a highly poisonous compound, it would be dangerous to treat NaCN with acids without proper ventilation.

15.123 When the pH is 10.00, the pOH is 4.00 and the concentration of hydroxide ion is $1.0 \times 10^{-4} M$. The concentration of HCN must be the same. (Why?) If the concentration of NaCN is x , the table looks like:

	$\text{CN}^-(aq)$	$+ \text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{HCN}(aq)$	$+$	$\text{OH}^-(aq)$
Initial (M):	x			0		0
Change (M):	-1.0×10^{-4}			$+1.0 \times 10^{-4}$		$+1.0 \times 10^{-4}$
Equilibrium (M):	$(x - 1.0 \times 10^{-4})$			(1.0×10^{-4})		(1.0×10^{-4})

$$K_b = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

$$2.0 \times 10^{-5} = \frac{(1.0 \times 10^{-4})^2}{(x - 1.0 \times 10^{-4})}$$

$$x = 6.0 \times 10^{-4} M = [\text{CN}^-]_0$$

$$\text{Amount of NaCN} = 250 \text{ mL} \times \frac{6.0 \times 10^{-4} \text{ mol NaCN}}{1000 \text{ mL}} \times \frac{49.01 \text{ g NaCN}}{1 \text{ mol NaCN}} = 7.4 \times 10^{-3} \text{ g NaCN}$$

15.124 $\text{pH} = 2.53 = -\log[\text{H}^+]$

$$[\text{H}^+] = 2.95 \times 10^{-3} M$$

Since the concentration of H^+ at equilibrium is $2.95 \times 10^{-3} M$, that means that $2.95 \times 10^{-3} M$ HCOOH ionized. Let' represent the initial concentration of HCOOH as I . The equation representing the ionization of formic acid is:

	$\text{HCOOH}(aq)$	\rightleftharpoons	$\text{H}^+(aq)$	$+$	$\text{HCOO}^-(aq)$
Initial (M):	I		0		0
Change (M):	-2.95×10^{-3}		$+2.95 \times 10^{-3}$		$+2.95 \times 10^{-3}$
Equilibrium (M):	$I - (2.95 \times 10^{-3})$		2.95×10^{-3}		2.95×10^{-3}

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

$$1.7 \times 10^{-4} = \frac{(2.95 \times 10^{-3})^2}{I - (2.95 \times 10^{-3})}$$

$$I = 0.054 M$$

There are 0.054 moles of formic acid in 1000 mL of solution. The mass of formic acid in 100 mL is:

$$100 \text{ mL} \times \frac{0.054 \text{ mol formic acid}}{1000 \text{ mL soln}} \times \frac{46.03 \text{ g formic acid}}{1 \text{ mol formic acid}} = \mathbf{0.25 \text{ g formic acid}}$$

15.125 The equilibrium is established:

	$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{CH}_3\text{COO}^-(aq) + \text{H}^+(aq)$		
Initial (M):	0.150	0	0.100
Change (M):	-x	+x	+x
Equilibrium (M):	(0.150 - x)	x	(0.100 + x)

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

$$1.8 \times 10^{-5} = \frac{x(0.100 + x)}{0.150 - x} \approx \frac{0.100x}{0.150}$$

$$x = 2.7 \times 10^{-5} M$$

$2.7 \times 10^{-5} M$ is the $[\text{H}^+]$ contributed by CH_3COOH . HCl is a strong acid that completely ionizes. It contributes a $[\text{H}^+]$ of $0.100 M$ to the solution.

$$[\text{H}^+]_{\text{total}} = [0.100 + (2.7 \times 10^{-5})] M \approx 0.100 M$$

$$\mathbf{\text{pH} = 1.000}$$

The pH is totally determined by the HCl and is independent of the CH_3COOH .

15.126 The balanced equation is: $\text{Mg} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2$

$$\text{mol of Mg} = 1.87 \text{ g Mg} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g Mg}} = 0.0769 \text{ mol}$$

From the balanced equation:

$$\text{mol of HCl required for reaction} = 2 \times \text{mol Mg} = (2)(0.0769 \text{ mol}) = 0.154 \text{ mol HCl}$$

The concentration of HCl:

$$\text{pH} = -0.544, \text{ thus } [\text{H}^+] = 3.50 M$$

$$\text{initial mol HCl} = M \times \text{Vol (L)} = (3.50 M)(0.0800 \text{ L}) = 0.280 \text{ mol HCl}$$

Moles of HCl left after reaction:

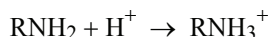
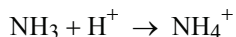
$$\text{initial mol HCl} - \text{mol HCl reacted} = 0.280 \text{ mol} - 0.154 \text{ mol} = 0.126 \text{ mol HCl}$$

Molarity of HCl left after reaction:

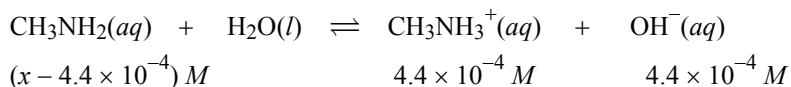
$$M = \text{mol/L} = 0.126 \text{ mol}/0.080 \text{ L} = 1.58 \text{ M}$$

$$\text{pH} = -\log(1.58) = -0.20$$

- 15.127** (a) The pH of the solution of HA would be lower. (Why?)
 (b) The electrical conductance of the HA solution would be greater. (Why?)
 (c) The rate of hydrogen evolution from the HA solution would be greater. Presumably, the rate of the reaction between the metal and hydrogen ion would depend on the hydrogen ion concentration (i.e., this would be part of the rate law). The hydrogen ion concentration will be greater in the HA solution.
- 15.128** The important equation is the hydrolysis of NO_2^- : $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$
- (a) Addition of HCl will result in the reaction of the H^+ from the HCl with the OH^- that was present in the solution. The OH^- will effectively be removed and the equilibrium will **shift to the right** to compensate (more hydrolysis).
 (b) Addition of NaOH is effectively addition of more OH^- which places stress on the right hand side of the equilibrium. The equilibrium will **shift to the left** (less hydrolysis) to compensate for the addition of OH^- .
 (c) Addition of NaCl will have **no effect**.
 (d) Recall that the percent ionization of a weak acid increases with dilution (see Figure 15.4 of the text). The same is true for weak bases. Thus dilution will cause more hydrolysis, shifting the equilibrium to the **right**.
- 15.129** Like carbon dioxide, sulfur dioxide behaves as a Lewis acid by accepting a pair of electrons from the Lewis base water. The Lewis acid-base adduct rearranges to form sulfurous acid in a manner exactly analogous to the rearrangement of the carbon dioxide-water adduct to form carbonic acid that is presented on page 683 of the textbook.
- 15.130** In Chapter 11, we found that salts with their formal electrostatic intermolecular attractions had low vapor pressures and thus high boiling points. Ammonia and its derivatives (amines) are molecules with dipole-dipole attractions; as long as the nitrogen has one direct N-H bond, the molecule will have hydrogen bonding. Even so, these molecules will have much higher vapor pressures than ionic species. Thus, if we could convert the neutral ammonia-type molecules into salts, their vapor pressures, and thus associated odors, would decrease. Lemon juice contains acids which can react with neutral ammonia-type (amine) molecules to form ammonium salts.



- 15.131** pH = 10.64
 pOH = 3.36
 $[\text{OH}^-] = 4.4 \times 10^{-4} \text{ M}$



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

$$4.4 \times 10^{-4} = \frac{(4.4 \times 10^{-4})(4.4 \times 10^{-4})}{x - (4.4 \times 10^{-4})}$$

$$4.4 \times 10^{-4}x - 1.9 \times 10^{-7} = 1.9 \times 10^{-7}$$

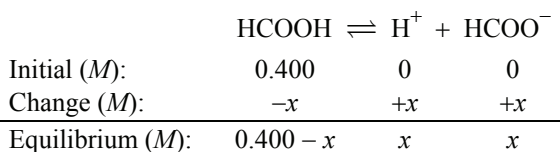
$$x = 8.6 \times 10^{-4} M$$

The molar mass of CH_3NH_2 is 31.06 g/mol.

The mass of CH_3NH_2 in 100.0 mL is:

$$100.0 \text{ mL} \times \frac{8.6 \times 10^{-4} \text{ mol CH}_3\text{NH}_2}{1000 \text{ mL}} \times \frac{31.06 \text{ g CH}_3\text{NH}_2}{1 \text{ mol CH}_3\text{NH}_2} = 2.7 \times 10^{-3} \text{ g CH}_3\text{NH}_2$$

15.132



Total concentration of particles in solution: $(0.400 - x) + x + x = 0.400 + x$

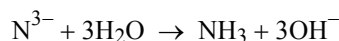
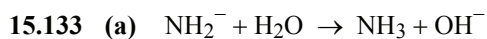
Assuming the molarity of the solution is equal to the molality, we can write:

$$\Delta T_f = K_f m$$

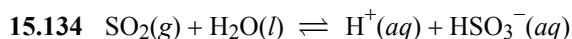
$$0.758 = (1.86)(0.400 + x)$$

$$x = 0.00753 = [\text{H}^+] = [\text{HCOO}^-]$$

$$K_a = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{(0.00753)(0.00753)}{0.400 - 0.00753} = 1.4 \times 10^{-4}$$



(b) N^{3-} is the stronger base since each ion produces 3 OH^- ions.



Recall that 0.12 ppm SO_2 would mean 0.12 parts SO_2 per 1 million (10^6) parts of air by volume. The number of particles of SO_2 per volume will be directly related to the pressure.

$$P_{\text{SO}_2} = \frac{0.12 \text{ parts SO}_2}{10^6 \text{ parts air}} \text{ atm} = 1.2 \times 10^{-7} \text{ atm}$$

We can now calculate the $[\text{H}^+]$ from the equilibrium constant expression.

$$K = \frac{[\text{H}^+][\text{HSO}_3^-]}{P_{\text{SO}_2}}$$

$$1.3 \times 10^{-2} = \frac{x^2}{1.2 \times 10^{-7}}$$

$$x^2 = (1.3 \times 10^{-2})(1.2 \times 10^{-7})$$

$$x = 3.9 \times 10^{-5} \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log(3.9 \times 10^{-5}) = \mathbf{4.40}$$

$$15.135 \quad \frac{[\text{H}^+][\text{ClO}^-]}{[\text{HClO}]} = 3.0 \times 10^{-8}$$

A pH of 7.8 corresponds to $[\text{H}^+] = 1.6 \times 10^{-8} \text{ M}$

Substitute $[\text{H}^+]$ into the equation above to solve for the $\frac{[\text{ClO}^-]}{[\text{HClO}]}$ ratio.

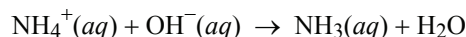
$$\frac{[\text{ClO}^-]}{[\text{HClO}]} = \frac{3.0 \times 10^{-8}}{1.6 \times 10^{-8}} = 1.9$$

This indicates that to obtain a pH of 7.8, the $[\text{ClO}^-]$ must be 1.9 times greater than the $[\text{HClO}]$. We can write:

$$\% \text{ClO}^- = \frac{\text{part ClO}^-}{\text{part ClO}^- + \text{part HClO}} \times 100\% = \frac{1.9}{1.9 + 1.0} \times 100\% = \mathbf{66\%}$$

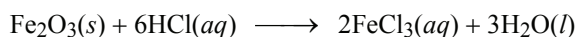
By difference, $\% \text{HClO} = \mathbf{34\%}$

15.136 In inhaling the smelling salt, some of the powder dissolves in the basic solution. The ammonium ions react with the base as follows:

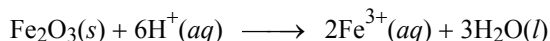


It is the pungent odor of ammonia that prevents a person from fainting.

15.137 (a) The overall equation is

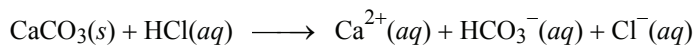


and the net ionic equation is

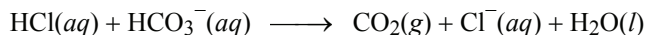


Since HCl donates the H^+ ion, it is the Brønsted acid. Each Fe_2O_3 unit accepts six H^+ ions; therefore, it is the Brønsted base.

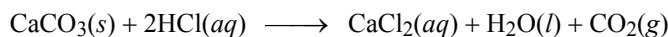
(b) The first stage is



and the second stage is



The overall equation is



The CaCl_2 formed is soluble in water.

(c) We need to find the concentration of the HCl solution in order to determine its pH. Let's assume a volume of 1.000 L = 1000 mL. The mass of 1000 mL of solution is:

$$1000 \text{ mL} \times \frac{1.073 \text{ g}}{1 \text{ mL}} = 1073 \text{ g}$$

The number of moles of HCl in a 15 percent solution is:

$$\frac{15\% \text{ HCl}}{100\% \text{ soln}} \times 1073 \text{ g soln} = (1.6 \times 10^2 \text{ g HCl}) \times \frac{1 \text{ mol HCl}}{36.46 \text{ g HCl}} = 4.4 \text{ mol HCl}$$

Thus, there are 4.4 moles of HCl in one liter of solution, and the concentration is 4.4 M. The pH of the solution is

$$\text{pH} = -\log(4.4) = \mathbf{-0.64}$$

This is a highly acidic solution (note that the pH is negative), which is needed to dissolve large quantities of rocks in the oil recovery process.

15.138 (c) does not represent a Lewis acid-base reaction. In this reaction, the F–F single bond is broken and single bonds are formed between P and each F atom. For a Lewis acid-base reaction, the Lewis acid is an electron-pair acceptor and the Lewis base is an electron-pair donor.

15.139 (a) False. A Lewis acid such as CO_2 is not a Brønsted acid. It does not have a hydrogen ion to donate.

(b) False. Consider the weak acid, NH_4^+ . The conjugate base of this acid is NH_3 , which is neutral.

(c) False. The percent ionization of a base decreases with increasing concentration of base in solution.

(d) False. A solution of barium fluoride is basic. The fluoride ion, F^- , is the conjugate base of a weak acid. It will hydrolyze to produce OH^- ions.

15.140 From the given pH's, we can calculate the $[\text{H}^+]$ in each solution.

$$\text{Solution (1): } [\text{H}^+] = 10^{-\text{pH}} = 10^{-4.12} = 7.6 \times 10^{-5} \text{ M}$$

$$\text{Solution (2): } [\text{H}^+] = 10^{-5.76} = 1.7 \times 10^{-6} \text{ M}$$

$$\text{Solution (3): } [\text{H}^+] = 10^{-5.34} = 4.6 \times 10^{-6} \text{ M}$$

We are adding solutions (1) and (2) to make solution (3). The volume of solution (2) is 0.528 L. We are going to add a given volume of solution (1) to solution (2). Let's call this volume x . The moles of H^+ in solutions (1) and (2) will equal the moles of H^+ in solution (3).

$$\text{mol H}^+ \text{ soln (1)} + \text{mol H}^+ \text{ soln (2)} = \text{mol H}^+ \text{ soln (3)}$$

Recall that $\text{mol} = M \times L$. We have:

$$(7.6 \times 10^{-5} \text{ mol/L})(x \text{ L}) + (1.7 \times 10^{-6} \text{ mol/L})(0.528 \text{ L}) = (4.6 \times 10^{-6} \text{ mol/L})(0.528 + x)\text{L}$$

$$(7.6 \times 10^{-5})x + (9.0 \times 10^{-7}) = (2.4 \times 10^{-6}) + (4.6 \times 10^{-6})x$$

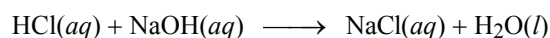
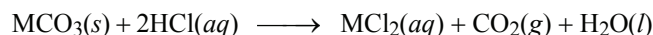
$$(7.1 \times 10^{-5})x = 1.5 \times 10^{-6}$$

$$x = 0.021 \text{ L} = \mathbf{21 \text{ mL}}$$

15.141 Given the equation: $\text{HbH}^+ + \text{O}_2 \rightleftharpoons \text{HbO}_2 + \text{H}^+$

- (a) From the equilibrium equation, high oxygen concentration puts stress on the left side of the equilibrium and thus shifts the concentrations to the right to compensate. **HbO₂** is favored.
- (b) High acid, H^+ concentration, places stress on the right side of the equation forcing concentrations on the left side to increase, thus releasing oxygen and increasing the concentration of **HbH⁺**.
- (c) Removal of CO_2 decreases H^+ (in the form of carbonic acid), thus shifting the reaction to the **right**. More HbO_2 will form. Breathing into a paper bag increases the concentration of CO_2 (re-breathing the exhaled CO_2), thus causing more O_2 to be released as explained above.

15.142 The balanced equations for the two reactions are:



First, let's find the number of moles of excess acid from the reaction with NaOH.

$$0.03280 \text{ L} \times \frac{0.588 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 0.0193 \text{ mol HCl}$$

The original number of moles of acid was:

$$0.500 \text{ L} \times \frac{0.100 \text{ mol HCl}}{1 \text{ L soln}} = 0.0500 \text{ mol HCl}$$

The amount of hydrochloric acid that reacted with the metal carbonate is:

$$(0.0500 \text{ mol HCl}) - (0.0193 \text{ mol HCl}) = 0.0307 \text{ mol HCl}$$

The mole ratio from the balanced equation is 1 mole MCO_3 : 2 mole HCl . The moles of MCO_3 that reacted are:

$$0.0307 \text{ mol HCl} \times \frac{1 \text{ mol MCO}_3}{2 \text{ mol HCl}} = 0.01535 \text{ mol MCO}_3$$

We can now determine the molar mass of MCO_3 , which will allow us to identify the metal.

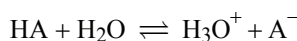
$$\text{molar mass MCO}_3 = \frac{1.294 \text{ g MCO}_3}{0.01535 \text{ mol MCO}_3} = 84.3 \text{ g/mol}$$

We subtract off the mass of CO_3^{2-} to identify the metal.

$$\text{molar mass M} = 84.3 \text{ g/mol} - 60.01 \text{ g/mol} = 24.3 \text{ g/mol}$$

The metal is **magnesium**.

15.143 We start with the equation for the hydrolysis of a weak acid.



At equilibrium, $[\text{H}_3\text{O}^+] = [\text{A}^-]$.

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

Because this is a weak acid, the concentration of HA at equilibrium is approximately equal to its initial concentration: $[\text{HA}] \approx [\text{HA}]_0$. Substituting into the above equation gives,

$$K_a \approx \frac{[\text{H}_3\text{O}^+]^2}{[\text{HA}]_0}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a[\text{HA}]_0}$$

By definition,

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_0} \times 100\% = \frac{\sqrt{K_a[\text{HA}]_0}}{[\text{HA}]_0} = \sqrt{\frac{K_a}{[\text{HA}]_0}}$$

Looking at this equation for % ionization, when $[\text{HA}]_0$ is decreased by a factor of 10 to $\frac{[\text{HA}]_0}{10}$, % ionization increases by $\sqrt{10}$. This result is in accord with LeChâtelier's principle, which predicts that ionization should increase with dilution.

15.144 Because HF is a much stronger acid than HCN, we can assume that the pH is largely determined by the ionization of HF.

	$\text{HF}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{F}^-(aq)$		
Initial (M):	1.00	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	1.00 - x	x	x

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

$$7.1 \times 10^{-4} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}$$

$$x = 0.027 M = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 1.57$$

HCN is a very weak acid, so at equilibrium, $[\text{HCN}] \approx 1.00 M$.

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

$$4.9 \times 10^{-10} = \frac{(0.027)[\text{CN}^-]}{1.00}$$

$$[\text{CN}^-] = 1.8 \times 10^{-8} M$$

In a 1.00 M HCN solution, the concentration of $[\text{CN}^-]$ would be:

	$\text{HCN}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{CN}^-(aq)$		
Initial (M):	1.00	0	0
Change (M):	-x	+x	+x
Equilibrium (M):	$1.00 - x$	x	x

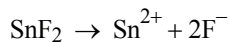
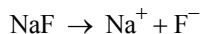
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$4.9 \times 10^{-10} = \frac{x^2}{1.00 - x} \approx \frac{x^2}{1.00}$$

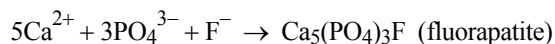
$$x = 2.2 \times 10^{-5} M = [\text{CN}^-]$$

$[\text{CN}^-]$ is greater in the 1.00 M HCN solution compared to the 1.00 M HCN/1.00 M HF solution. According to LeChâtelier's principle, the high $[\text{H}_3\text{O}^+]$ (from HF) shifts the HCN equilibrium from right to left decreasing the ionization of HCN. The result is a smaller $[\text{CN}^-]$ in the presence of HF.

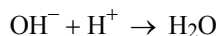
15.145 Both NaF and SnF_2 provide F^- ions in solution.



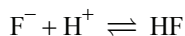
Because HF is a much stronger acid than H_2O , it follows that F^- is a much weaker base than OH^- . The F^- ions replace OH^- ions during the remineralization process



because OH^- has a much greater tendency to combine with H^+



than F^- does.

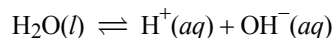


Because F^- is a weaker base than OH^- , fluorapatite is more resistant to attacks by acids compared to hydroxyapatite.

- 15.146** The van't Hoff equation allows the calculation of an equilibrium constant at a different temperature if the value of the equilibrium constant at another temperature and ΔH° for the reaction are known.

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

First, we calculate ΔH° for the ionization of water using data in Appendix 3 of the text.



$$\Delta H^\circ = [\Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{OH}^-)] - \Delta H_f^\circ(\text{H}_2\text{O})$$

$$\Delta H^\circ = (0 - 229.94 \text{ kJ/mol}) - (-285.8 \text{ kJ/mol})$$

$$\Delta H^\circ = 55.9 \text{ kJ/mol}$$

We substitute ΔH° and the equilibrium constant at 25°C (298 K) into the van't Hoff equation to solve for the equilibrium constant at 100°C (373 K).

$$\ln \frac{1.0 \times 10^{-14}}{K_2} = \frac{55.9 \times 10^3 \text{ J/mol}}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{373 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\frac{1.0 \times 10^{-14}}{K_2} = e^{-4.537}$$

$$K_2 = 9.3 \times 10^{-13}$$

We substitute into the equilibrium constant expression for the ionization of water to solve for $[\text{H}^+]$ and then pH.

$$K_2 = [\text{H}^+][\text{OH}^-]$$

$$9.3 \times 10^{-13} = x^2$$

$$x = [\text{H}^+] = 9.6 \times 10^{-7} \text{ M}$$

$$\text{pH} = -\log(9.6 \times 10^{-7}) = \mathbf{6.02}$$

Note that the water is **not** acidic at 100°C because $[\text{H}^+] = [\text{OH}^-]$.