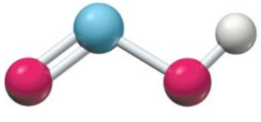
WORKED EXAMPLE 14.1 Explaining Acidity with the Arrhenius and Brønsted–Lowry Theories

Account for the acidic properties of nitrous acid (HNO_2) in terms of the Arrhenius theory and the Brønsted–Lowry theory, and identify the conjugate base of HNO_2.



Nitrous acid

Strategy

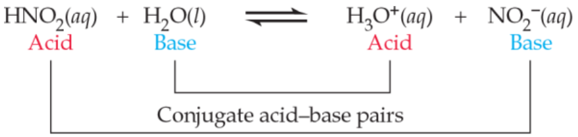
To account for the acidity of a substance, consider how it can produce H^+ ions in water (Arrhenius theory) and how it can act as a proton donor (Brønsted–Lowry theory).

Solution

HNO_2 is an Arrhenius acid because it dissociates in water to produce H^+ ions:

$$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$$

Nitrous acid is a Brønsted–Lowry acid because it acts as a proton donor when it dissociates, transferring a proton to water to give the hydronium ion, H_3O^+:



$$\underset{\text{Acid}}{HNO_2(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Acid}}{H_3O^+(aq)} + \underset{\text{Base}}{NO_2^-(aq)}$$

The conjugate base of HNO_2 is NO_2^-, the species that remains after HNO_2 has lost a proton.

PROBLEM 14.1 Write a balanced equation for the dissociation of each of the following Brønsted–Lowry acids in water:

(a) H_2SO_4 **(b)** HSO_4^- **(c)** H_3O^+ **(d)** NH_4^+

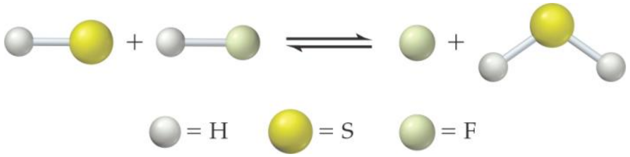
What is the conjugate base of each acid?

PROBLEM 14.2 What is the conjugate acid of each of the following Brønsted–Lowry bases?

(a) HCO_3^- **(b)** CO_3^{2-} **(c)** OH^- **(d)** $H_2PO_4^-$

WORKED KEY CONCEPT EXAMPLE 14.2 Identifying Brønsted–Lowry Acids, Bases, and Conjugate Acid–Base Pairs

For the following reaction in aqueous solution, identify the Brønsted–Lowry acids, bases, and conjugate acid–base pairs:

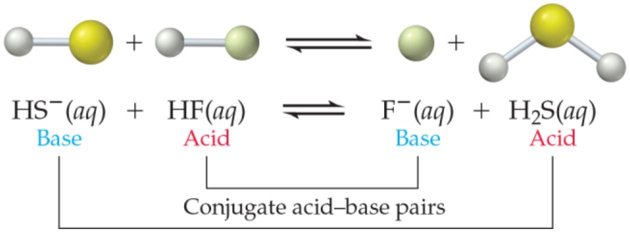


Strategy

The simplest approach is to identify the conjugate acid–base pairs, the species whose formulas differ by just one proton.

Solution

The second reactant is HF, and the first product is its conjugate base F^-. The second product is H_2S, and the first reactant is its conjugate base HS^-. Therefore, the Brønsted–Lowry acids, bases, and conjugate acid–base pairs are as follows:

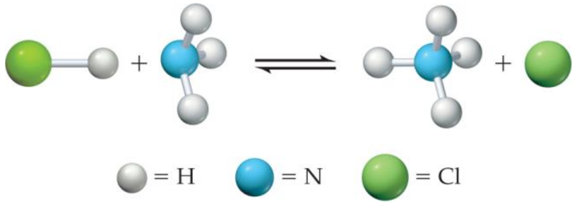


$$HS^-(aq) + HF(aq) \rightleftharpoons F^-(aq) + H_2S(aq)$$

WORKED KEY CONCEPT EXAMPLE 14.2 Identifying Brønsted–Lowry Acids, Bases, and Conjugate Acid–Base Pairs

Continued

KEY CONCEPT PROBLEM 14.3 For the following reaction in aqueous solution, identify the Brønsted–Lowry acids, bases, and conjugate acid–base pairs:



WORKED EXAMPLE 14.3 Predicting the Direction of Acid–Base Reactions

If you mix equal concentrations of reactants and products, which of the following reactions proceed to the right and which proceed to the left?

(a) $H_2SO_4(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + HSO_4^-(aq)$

(b) $HCO_3^-(aq) + SO_4^{2-}(aq) \rightleftharpoons HSO_4^-(aq) + CO_3^{2-}(aq)$

Strategy

To predict the direction of reaction, use the balanced equation to identify the acids and bases, and then use Table 14.1 to identify the stronger acid and the stronger base. When equal concentrations of reactants and products are present, proton transfer always occurs from the stronger acid to the stronger base.

Solution

(a) In this reaction, H_2SO_4 and NH_4^+ are the acids, and NH_3 and HSO_4^- are the bases. According to Table 14.1, H_2SO_4 is a stronger acid than NH_4^+, and NH_3 is a stronger base than HSO_4^-. Therefore, NH_3 gets the proton and the reaction proceeds from left to right.

$$\underset{\text{Stronger acid}}{H_2SO_4(aq)} + \underset{\text{Stronger base}}{NH_3(aq)} \longrightarrow \underset{\text{Weaker acid}}{NH_4^+(aq)} + \underset{\text{Weaker base}}{HSO_4^-(aq)}$$

(b) HCO_3^- and HSO_4^- are the acids, and SO_4^{2-} and CO_3^{2-} are the bases. Table 14.1 indicates that HSO_4^- is the stronger acid and CO_3^{2-} is the stronger base. Therefore, CO_3^{2-} gets the proton and the reaction proceeds from right to left.

$$\underset{\text{Weaker acid}}{HCO_3^-(aq)} + \underset{\text{Weaker base}}{SO_4^{2-}(aq)} \longleftarrow \underset{\text{Stronger acid}}{HSO_4^-(aq)} + \underset{\text{Stronger base}}{CO_3^{2-}(aq)}$$

WORKED EXAMPLE 14.3 Predicting the Direction of Acid–Base Reactions

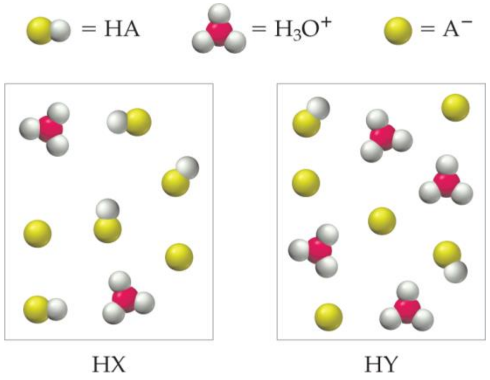
Continued

PROBLEM 14.4 If you mix equal concentrations of reactants and products, which of the following reactions proceed to the right and which proceed to the left?

(a) $HF(aq) + NO_3^-(aq) \rightleftharpoons HNO_3(aq) + F^-(aq)$

(b) $NH_4^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + NH_3(aq)$

KEY CONCEPT PROBLEM 14.5 The following pictures represent aqueous solutions of two acids HA (A = X or Y); water molecules have been omitted for clarity.



(a) Which is the stronger acid, HX or HY?

(b) Which is the stronger base, X^- or Y^-?

(c) If you mix equal concentrations of reactants and products, will the following reaction proceed to the right or to the left?

$$HX + Y^- \rightleftharpoons HY + X^-$$

WORKED EXAMPLE 14.4 Calculating $[OH^-]$ from K_w and $[H_3O^+]$

The concentration of H_3O^+ ions in a sample of lemon juice is 2.5×10^{-3} M. Calculate the concentration of OH^- ions, and classify the solution as acidic, neutral, or basic.

Strategy

When $[H_3O^+]$ is known, the concentration can be found from the expression $[OH^-] = Kw/[H_3O^+]$.

Solution

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-3}} = 4.0 \times 10^{-12}\ \text{M}$$

Because $[H_3O^+] > [OH^-]$, the solution is acidic.

Ballpark Check

Because the product of the H_3O^+ and OH^- concentrations must equal 10^{-14}, and because the H_3O^+ concentration is in the range 10^{-3} M to 10^{-2} M the OH^- concentration must be in the range 10^{-11} M to 10^{-12} M. The ballpark check and the solution agree.

PROBLEM 14.6 The concentration of OH^- in a sample of seawater is 5.0×10^{-6} M. Calculate the concentration of H_3O^+ ions, and classify the solution as acidic, neutral, or basic.

PROBLEM 14.7 At 50° C the value of is Kw is 5.5×10^{-14}. What are the concentrations of H_3O^+ and OH^- in a neutral solution at 50° C?

WORKED EXAMPLE 14.5 Calculating the pH from the H_3O^+ Concentration

Calculate the pH of an aqueous ammonia solution that has an OH^- concentration of 1.9×10^{-3} M.

Strategy

First, calculate the H_3O^+ concentration from the OH^- concentration, and then take the negative logarithm of $[H_3O^+]$ to convert to pH.

Solution

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-3}} = 5.3 \times 10^{-12}\ \text{M}$$

$$\text{pH} = -\log\,[H_3O^+] = -\log\,(5.3 \times 10^{-12}) = 11.28$$

The pH is quoted to two significant figures (0.28) because $[H_3O^+]$ is known to two significant figures (5.3).

Ballpark Check

Because $[OH^-]$ is between 10^{-3} M and 10^{-2} M, $[H_2O^+]$ is between 10^{-11} M and 10^{-12} M. Therefore, the pH is between 11 and 12, in agreement with the solution.

WORKED EXAMPLE 14.6 Calculating the H_3O^+ Concentration from the pH

Acid rain is a matter of serious concern because most species of fish die in waters having a pH lower than 4.5–5.0. Calculate the H_3O^+ concentration in a lake that has a pH of 4.5.

Strategy

Calculate the H_3O^+ concentration by taking the antilogarithm of the negative of the pH.

Solution

$$[H_3O^+] = \text{antilog}(-\text{pH}) = 10^{-\text{pH}} = 10^{-4.5} = 3 \times 10^{-5}\ \text{M}$$

$[H_3O^+]$ is reported to only one significant figure because the pH has only one digit beyond the decimal point. (If you need help in finding the antilog of a number, see Appendix A.2.)

Ballpark Check

Because a pH of 4.5 is between 4 and 5, $[H_3O^+]$ is between 10^{-4} M and 10^{-5} M, in agreement with the solution.

PROBLEM 14.8 Calculate the pH of each of the following solutions:
(a) A sample of seawater that has OH^- an concentration of 1.58×10^{-6} M
(b) A sample of acid rain that has an H_3O^+ concentration of 6.0×10^{-5} M

PROBLEM 14.9 Calculate the concentrations of H_3O^+ and OH^- in each of the following solutions:
(a) Human blood (pH 7.40) **(b)** A cola beverage (pH 2.8)

WORKED EXAMPLE 14.7 Calculating the pH of a Strong Acid Solution

Calculate the pH of a 0.025 M HNO_3 solution.

Strategy

Because nitric acid is a strong acid, it is almost completely dissociated in aqueous solution. Therefore, the $[H_3O^+]$ equals the initial concentration of the HNO_3, and the pH equals the negative log of the $[H_3O^+]$.

Solution

$$HNO_3(aq) + H_2O(l) \xrightarrow{100\%} H_3O^+(aq) + NO_3^-(aq)$$

$$pH = -\log [H_3O^+] = -\log (2.5 \times 10^{-2}) = 1.60$$

Ballpark Check

Because the $[H_3O^+]$ is between 10^{-1} M and 10^{-2} M, the pH is between 1 and 2, in agreement with the solution.

WORKED EXAMPLE 14.8 Calculating the pH of a Strong Base Solution

Calculate the pH of each of the following solutions:

(a) A 0.10 M solution of NaOH

(b) A 0.0050 M solution of slaked lime [$Ca(OH)_2$]

(c) A solution prepared by dissolving 0.28 g of lime (CaO) in enough water to make 1.00 L of limewater [$Ca(OH)_2(aq)$]

Strategy

Because NaOH and $Ca(OH)_2$ are strong bases, they are essentially 100% dissociated and their [OH^-] is directly related to their initial concentrations. To calculate the [OH^-] in a solution prepared by dissolving CaO, we must first do a mass-to-mole conversion and then use the balanced equation for the reaction of CaO with water to find the number of moles of OH^- in the solution. In each case, $[H_3O^+] = Kw/[OH^-]$ and $pH = -\log [H_3O^+]$.

Solution

(a) Because NaOH is a strong base, $[OH^-] = 0.10$ M, $[H_3O^+] = 1.0 \times 10^{-13}$ M, and pH = 13.00.

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\ M$$

$$pH = -\log(1.0 \times 10^{-13}) = 13.00$$

(b) Because slaked lime is a strong base, it provides 2 OH^- ions per $Ca(OH)_2$ formula unit. Therefore, $[OH^-] = 2(0.0050\ M)$, $[H_3O^+] = 1.0 \times 10^{-12}$ M, and pH = 12.00:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12}\ M$$

$$pH = -\log(1.0 \times 10^{-12}) = 12.00$$

WORKED EXAMPLE 14.8 Calculating the pH of a Strong Base Solution

Continued

(c) First calculate the number of moles of CaO dissolved from the given mass of CaO and its molar mass (56.1 g/mol):

$$\text{Moles of CaO} = 0.28\text{ g CaO} \times \frac{1\text{ mol CaO}}{56.1\text{ g CaO}} = 0.0050\text{ mol CaO}$$

Protonation of the O^{2-} ion produces 2 mol of OH^- per mole of CaO dissolved:

$$CaO(s) + H_2O(l) \longrightarrow Ca^{2+}(aq) + 2\ OH^-(aq)$$

$$\text{Moles of }OH^-\text{ produced} = 2(0.0050\text{ mol}) = 0.010\text{ mol}$$

Since the solution volume is 1.00 L,

$$[OH^-] = \frac{0.010\text{ mol}}{1.00\text{ L}} = 0.010\text{ M}$$

The $[OH^-]$ happens to be identical to that in part **(b)**. Therefore, pH = 12.00.

PROBLEM 14.10 Calculate the pH of the following solutions:

(a) 0.050 M $HCIO_4$

(b) 6.0 M HCl

(c) 4.0 M KOH

(d) 0.010 M $Ba(OH)_2$

PROBLEM 14.11 Calculate the pH of a solution prepared by dissolving 0.25 g of BaO in enough water to make 0.500 L of solution.

WORKED EXAMPLE 14.9 Calculating K_a and pK_a for a Weak Acid from the pH of the Solution

The pH of 0.250 M HF is 2.036. What are the values of K_a and pK_a for hydrofluoric acid?

Strategy

First, write the balanced equation for the dissociation equilibrium. Then, define x as the concentration of HF that dissociates and make the usual table under the balanced equation (Figure 13.6, Steps 1 and 2). Because x equals the H_3O^+ concentration, its value can be calculated from the pH. Finally, substitute the equilibrium concentrations into the equilibrium equation to obtain the value of K_a and take the negative log of K_a to obtain the pK_a.

Solution

	$HF(aq)$ +	$H_2O(l) \rightleftharpoons$	$H_3O^+(aq)$ +	$F^-(aq)$
Initial concentration (M)	0.250		~0*	0
Change (M)	$-x$		$+x$	$+x$
Equilibrium concentration (M)	$(0.250 - x)$		x	x

*A very small concentration of H_3O^+ is present initially because of the dissociation of water.

We can calculate the value of x from the pH:

$$x = [H_3O^+] = \text{antilog}(-\text{pH}) = 10^{-\text{pH}} = 10^{-2.036} = 9.20 \times 10^{-3}\ \text{M}$$

The other equilibrium concentrations are

$$[F^-] = x = 9.20 \times 10^{-3}\ \text{M}$$

$$[HF] = 0.250 - x = 0.250 - 0.00920 = 0.241\ \text{M}$$

Substituting these concentrations into the equilibrium equation gives the value of Ka:

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{(0.250 - x)} = \frac{(9.20 \times 10^{-3})(9.20 \times 10^{-3})}{0.241} = 3.51 \times 10^{-4}$$

$$pK_a = -\log K_a = -\log (3.51 \times 10^{-4}) = 3.455$$

Ballpark Check

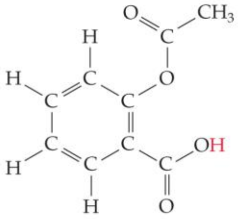
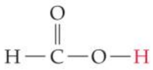
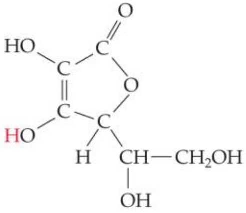
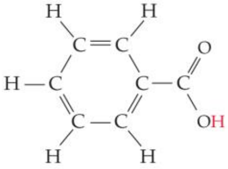
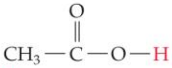
Because the pH is about 2, $[H_3O^+]$ and $[F^-]$ are about 10^{-2} M, and [HF] is about 0.25 M (0.250 M – 10^{-2} M). The value of K_a is therefore about $(10^{-2})\ (10^{-2})/0.25$, or 4×10^{-4}, and the pK_a is between 3 and 4. The ballpark check and the solution agree.

WORKED EXAMPLE 14.9 Calculating K_a and pK_a for a Weak Acid from the pH of the Solution

Continued

PROBLEM 14.12 The pH of 0.10 M HOCl is 4.23. Calculate K_a and pK_a for hypochlorous acid, and check your answers against the values given in Table 14.2.

TABLE 14.2 Acid–Dissociation Constants at 25 °C

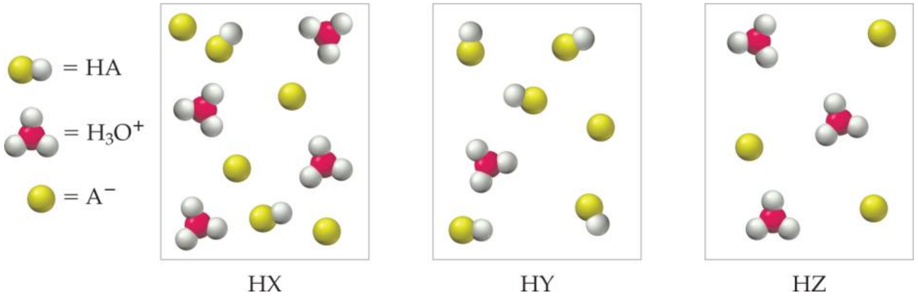
	Acid	Molecular Formula	Structural Formula*	K_a	pK_a†
Stronger acid 	Hydrochloric	HCl	H—Cl	2×10^{6}	−6.3
	Nitrous	HNO_2	H—O—N=O	4.5×10^{-4}	3.35
	Hydrofluoric	HF	H—F	3.5×10^{-4}	3.46
	Acetylsalicylic (aspirin)	$C_9H_8O_4$		$3.0 \times 10^{--4}$	3.52
	Formic	HCO_2H	 $H-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Benzoic	$C_6H_5CO_2H$		6.5×10^{-5}	4.19
	Acetic	CH_3CO_2H	 $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$	1.8×10^{-5}	4.74
	Hypochlorous	$HOCl$	H—O—Cl	3.5×10^{-8}	7.46
	Hydrocyanic	HCN	H—C≡N	4.9×10^{-10}	9.31
Weaker acid	Methanol	CH_3OH	CH_3—O—H	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in red. †pK_a = −log K_a.

WORKED EXAMPLE 14.9 Calculating K_a and pK_a for a Weak Acid from the pH of the Solution

Continued

KEY CONCEPT PROBLEM 14.13 The following pictures represent aqueous solutions of three acids HA (A = X, Y, or Z); water molecules have been omitted for clarity:



(a) Arrange the three acids in order of increasing value of K_a.
(b) Which acid, if any, is a strong acid?
(c) Which solution has the highest pH, and which has the lowest pH?

WORKED EXAMPLE 14.10 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Acid

Calculate the pH and the concentrations of all species present (H_3O^+, F^-, HF, and OH^-) in 0.050 M HF.

Strategy

Follow the eight-step sequence outlined in Figure 14.7.

Solution

Step 1 The species present initially are

HF	H_2O
Acid	Acid or base

Step 2 The possible proton-transfer reactions are

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \qquad K_a = 3.5 \times 10^{-4}$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

Step 3 Since $K_a >> Kw$, the principal reaction is the dissociation of HF.

Step 4

Principal Reaction:	$HF(aq)$	$+ H_2O(l) \rightleftharpoons$	$H_3O^+(aq)$	$+ F^-(aq)$
Initial concentration (M)	0.050		~0	0
Change (M)	$-x$		$+x$	$+x$
Equilibrium concentration (M)	$0.050 - x$		x	x

Step 5 Substituting the equilibrium concentrations into the equilibrium equation for the principal reaction gives

$$K_a = 3.5 \times 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]} = \frac{(x)(x)}{(0.050 - x)}$$

Making the usual approximation that x is negligible compared with the initial concentration of the acid we assume that $(0.050 - x) \approx 0.050$ and then solve for an approximate value of x:

WORKED EXAMPLE 14.10 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Acid

Continued

Making the usual approximation that x is negligible compared with the initial concentration of the acid we assume that $(0.050 - x) \approx 0.050$ and then solve for an approximate value of x:

$$x^2 \approx (3.5 \times 10^{-4})(0.050)$$

$$x \approx 4.2 \times 10^{-3}$$

Since the initial concentration of HF (0.050 M) is known to the third decimal place, x is negligible compared with the initial [HF] only if x is less than 0.001 M. Our approximate value of x(0.0042 M) is not negligible compared with 0.050 M because 0.050 M – 0.0042 M = 0.046 M. Therefore, our approximation, $0.050 - x \approx 0.050$, is invalid, and we must solve the quadratic equation without making approximations:

$$3.5 \times 10^{-4} = \frac{x^2}{(0.050 - x)}$$

$$x^2 + (3.5 \times 10^{-4})x - (1.75 \times 10^{-5}) = 0$$

We use the standard quadratic formula (Appendix A. 4):

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-(3.5 \times 10^{-4}) \pm \sqrt{(3.5 \times 10^{-4})^2 - 4(1)(-1.75 \times 10^{-5})}}{2(1)} \\ &= \frac{-(3.5 \times 10^{-4}) \pm (8.37 \times 10^{-3})}{2} \\ &= +4.0 \times 10^{-3} \quad \text{or} \quad -4.4 \times 10^{-3} \end{aligned}$$

Of the two solutions for x, only the positive value has physical meaning, since x is the H_3O^+ concentration. Therefore,

$$x = 4.0 \times 10^{-3}$$

Note that whether we must solve the quadratic equation depends on both the size of x and the number of significant figures in the initial concentration.

WORKED EXAMPLE 14.10 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Acid

Continued

Step 6 The big concentrations are

$$[H_3O^+] = [F^-] = x = 4.0 \times 10^{-3}\ M$$

$$[HF] = (0.050 - x) = (0.050 - 0.0040) = 0.046\ M$$

Step 7 The small concentration, $[OH^-]$, is obtained from the subsidiary equilibrium, the dissociation of water:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-3}} = 2.5 \times 10^{-12}\ M$$

Step 8 $pH = -\log[H_3O^+] = -\log(4.0 \times 10^{-3}) = 2.40$

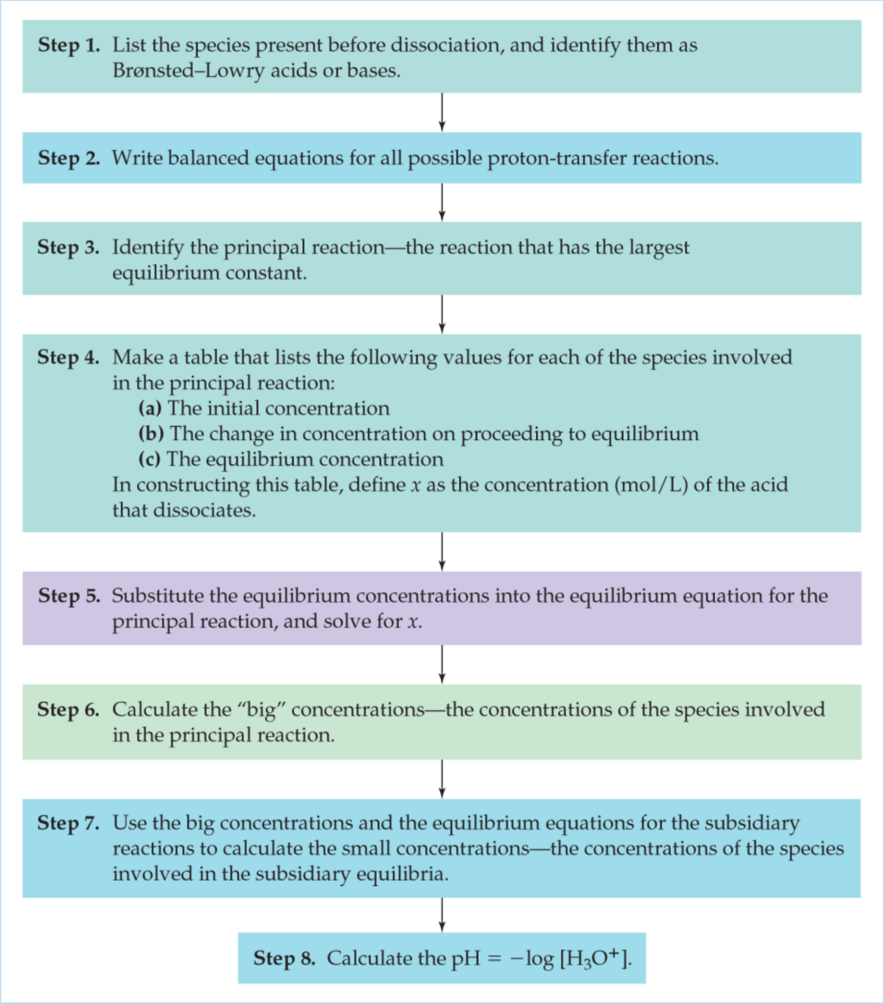
Ballpark Check

Arithmetic errors in solving quadratic equations are common, so it's a good idea to check that the value of x obtained from the quadratic equation is reasonable. If the approximate value of x (4.2×10^{-3}) is fairly small compared to the initial concentration of the acid (0.050 M), as is the case in this problem, then the value of x obtained from the quadratic equation (4.0×10^{-3}) should be fairly close to the approximate value of x. The approximate and more exact values of x agree.

WORKED EXAMPLE 14.10 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Acid

Continued

FIGURE 14.7
Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:
- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the “big” concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

Step 8. Calculate the pH $= -\log [H_3O^+]$.

WORKED EXAMPLE 14.10 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Acid

Continued

PROBLEM 14.14 Acetic acid, CH_3CO_2H, is the solute that gives vinegar its characteristic odor and sour taste. Calculate the pH and the concentrations of all species present (H_3O^+, $CH_3CO_2^-$, CH_3CO_2H, and OH^-) in:

(a) 1.00 M CH_3CO_2H
(b) 0.0100 M CH_3CO_2H

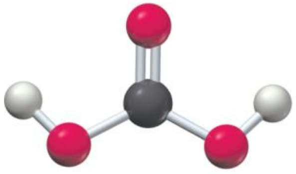
PROBLEM 14.15 A vitamin C tablet containing 250 mg of ascorbic acid ($C_6H_8O_6$; $K_a = 8.0 \times 10^{-5}$) is dissolved in a 250 mL glass of water. What is the pH of the solution?

WORKED EXAMPLE 14.11 Calculating the pH and the Equilibrium Concentrations in a Solution of a Diprotic Acid

Calculate the pH and the concentrations of all species present (H_2CO_3, HCO_3^-, CO_3^{2-}, H_3O^+, and OH^-) in a 0.020 M carbonic acid solution.

Strategy

Use the eight-step procedure summarized in Figure 14.7. The values of K_{a1} and K_{a2} may be found in Table 14.3.



Carbonic acid

Solution

Step 1–3 The species present initially are H_2CO_3 (acid) and H_2O (acid or base). Because $K_{a1} >> Kw$, the principal reaction is the dissociation of H_2CO_3.

Step 4

Principal Reaction	$H_2CO_3(aq) + H_2O(l) \rightleftharpoons$	$H_3O^+(aq) +$	$HCO_3^-(aq)$
Initial concentration (M)	0.020	~0	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.020 - x$	x	x

Step 5 Substituting the equilibrium concentrations into the equilibrium equation for the principal reaction gives

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = \frac{(x)(x)}{(0.020 - x)}$$

Assuming that $(0.020 - x) \approx 0.020$,

$$x^2 = (4.3 \times 10^{-7})(0.020)$$

$$x = 9.3 \times 10^{-5} \qquad \text{Approximation } (0.020 - x) \approx 0.020 \text{ is justified.}$$

Step 6 The big concentrations are

$$[H_3O^+] = [HCO_3^-] = x = 9.3 \times 10^{-5}\text{ M}$$

$$[H_2CO_3] = 0.020 - x = 0.020 - 0.000\,093 = 0.020\text{ M}$$

WORKED EXAMPLE 14.11 Calculating the pH and the Equilibrium Concentrations in a Solution of a Diprotic Acid

Continued

Step 7 The small concentrations are obtained from the subsidiary equilibria—(1) dissociation of HCO_3^- and (2) dissociation of water—and from the big concentrations already determined:

$$(1)\quad HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$$

$$K_{a2} = 5.6 \times 10^{-11} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{(9.3 \times 10^{-5})[CO_3^{2-}]}{9.3 \times 10^{-5}}$$

$$[CO_3^{2-}] = K_{a2} = 5.6 \times 10^{-11}\ \text{M}$$

(In general, for a solution of a weak diprotic acid that has a very small value of K_{a2}, $[A^{2-}] = K_{a2}$.)

$$(2)\quad [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{9.3 \times 10^{-5}} = 1.1 \times 10^{-10}\ \text{M}$$

The second dissociation of H_2CO_3 produces a negligible amount of H_3O^+ compared with the H_3O^+ obtained from the first dissociation. Of the 9.3×10^{-5}mol/L of HCO_3^- produced by the first dissociation, only 5.6×10^{-11}mol/L dissociates to form H_3O^+ and CO_3^{2-}.

Step 8 $\text{pH} = -\log[H_3O^+] = -\log(9.3 \times 10^{-5}) = 4.03$

Ballpark Check

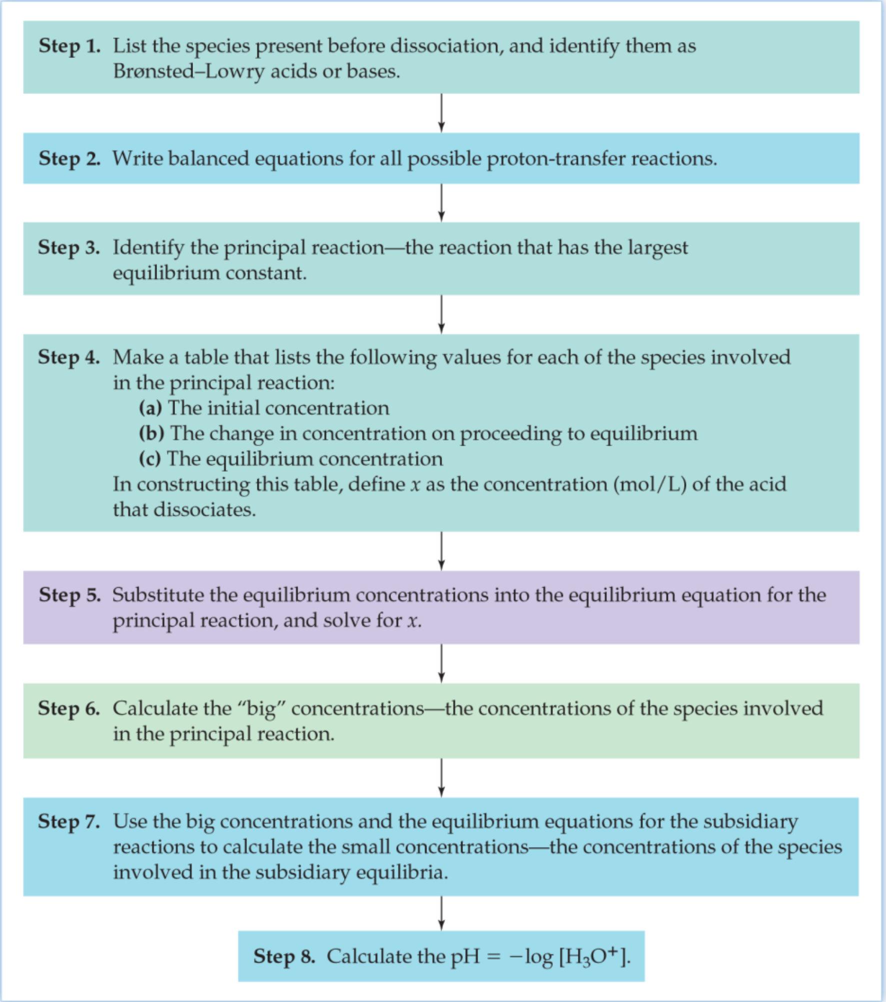
When the value of x can be neglected compared with the initial concentration of the acid (Step 5), the $[H_3O^+]$ equals the square root of the product of K_{a1} and the initial concentration of the acid. In this problem, $[H_3O^+]$ is the square root of approximately (4×10^{-7}), or about 10^{-4} M. Therefore, the pH ≈ 4, in agreement with the solution.

WORKED EXAMPLE 14.11 Calculating the pH and the Equilibrium Concentrations in a Solution of a Diprotic Acid

Continued

FIGURE 14.7

Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:
- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the "big" concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

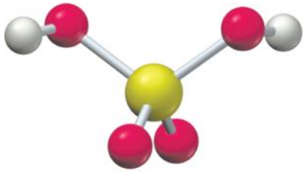
Step 8. Calculate the pH = $-\log [H_3O^+]$.

WORKED EXAMPLE 14.12 Calculating the pH and the Equilibrium Concentrations in a Sulfuric Acid Solution

Calculate the pH and the concentrations of all species present (HSO_4^-, SO_4^{2-}, H_3O^+, and OH^-) in 0.10 M H_2SO_4.

Strategy

Use the eight-step procedure summarized in Figure 14.7.



Sulfuric acid

Solution

Step 1–3 Because H_2SO_4 is essentially 100% dissociated to give H_3O^+ and HSO_4^- (K_{a1} is very large), the species present initially are H_3O^+ (acid), HSO_4^- (acid), and H_2O (acid or base). Although H_3O^+ is the strongest acid present, proton transfer from H_3O^+ to H_2O to give H_2O and H_3O^+ is not considered to be the principal reaction because it does not change any of the concentrations. The next strongest acid present is HSO_4^- ($K_{a2} > K_w$), so we consider the principal reaction to be dissociation of HSO_4^-.

Step 4

Principal Reaction	$HSO_4^-(aq)$ + $H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$SO_4^{2-}(aq)$
Initial concentration (M)	0.10	0.10	0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.10 - x$	$0.10 + x$	x

Note that the second dissociation step takes place in the presence of 0.10 M H_3O^+ from the first dissociation step.

Step 5 Substituting the equilibrium concentrations into the equilibrium equation for the principal reaction gives

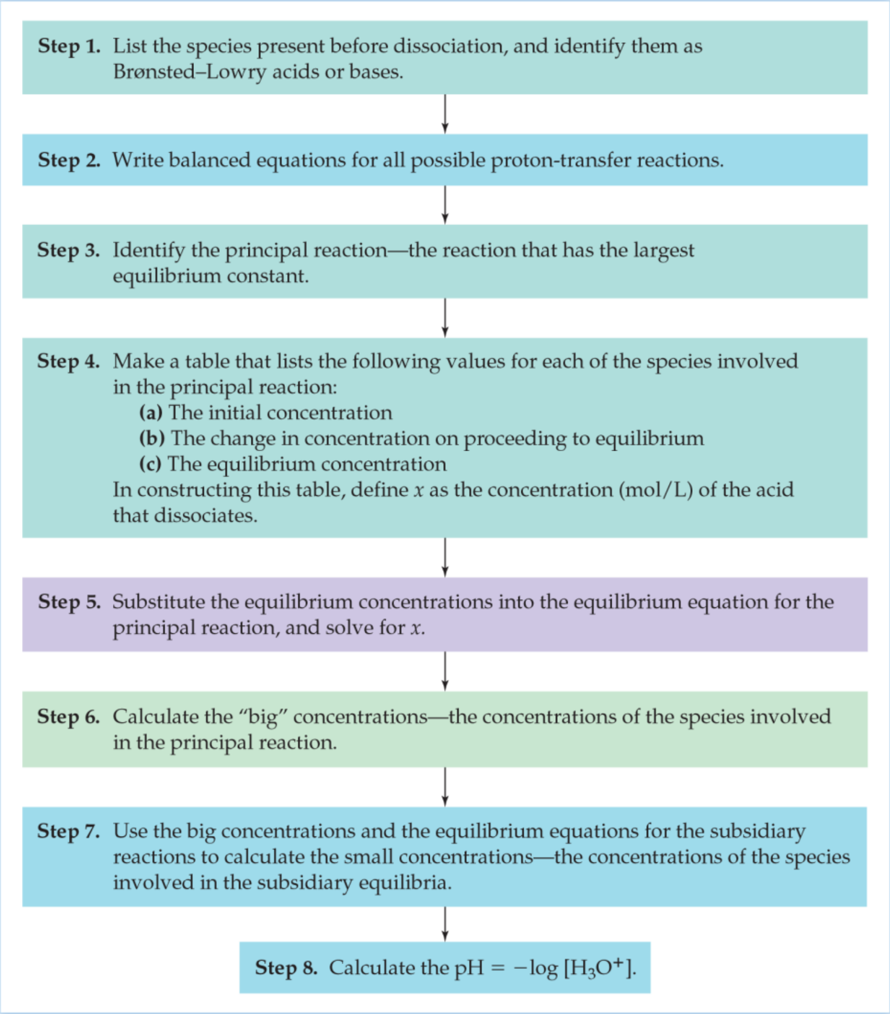
$$K_{a2} = 1.2 \times 10^{-2} = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.10 + x)(x)}{(0.10 - x)}$$

WORKED EXAMPLE 14.12 Calculating the pH and the Equilibrium Concentrations in a Sulfuric Acid Solution

Continued

FIGURE 14.7

Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:

- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the "big" concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

Step 8. Calculate the $pH = -\log [H_3O^+]$.

WORKED EXAMPLE 14.12 Calculating the pH and the Equilibrium Concentrations in a Sulfuric Acid Solution

Continued

Neglecting x compared with 0.10 and solving this equation would give $x = K_{a2} = 0.012$, which is not negligible compared with 0.10. Therefore, we use the quadratic equation to obtain the value of x:

$$0.0012 - 0.012x = 0.10x + x^2$$

$$x^2 + 0.112x - 0.0012 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.112 \pm \sqrt{(0.112)^2 - 4(1)(-0.0012)}}{2(1)}$$

$$= \frac{-0.112 \pm 0.132}{2}$$

$$= +0.010 \quad \text{or} \quad -0.122$$

Because x is the SO_4^{2-} concentration, it must be positive. Therefore,

$$x = 0.010$$

Step 6 The big concentrations are

$$[SO_4^{2-}] = x = 0.010\ \text{M}$$

$$[HSO_4^-] = 0.10 - x = 0.10 - 0.010 = 0.09\ \text{M}$$

$$[H_3O^+] = 0.10 + x = 0.10 + 0.010 = 0.11\ \text{M}$$

Step 7 The small concentration, $[OH^-]$, is obtained from the subsidiary equilibrium, dissociation of water:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{0.11} = 9.1 \times 10^{-14}\ \text{M}$$

Step 8 $pH = -\log [H_3O^+] = -\log 0.11 = 0.96$

WORKED EXAMPLE 14.12 Calculating the pH and the Equilibrium Concentrations in a Sulfuric Acid Solution

Continued

Ballpark Check

The easiest check in this case is to substitute the big concentrations obtained in Step 6 into the equilibrium equation for the second dissociation step and show that the equilibrium constant expression equals K_{a2}:

$$\frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(0.11)(0.010)}{0.09} = 0.012 = K_{a2}$$

Since $[H_3O^+]$ is approximately 10^{-1} M, the pH should be about 1, in agreement with the detailed solution.

PROBLEM 14.17 Calculate the pH and the concentrations of all species present in 0.10 M H_2SO_3. Values of K_a are in Table 14.3.

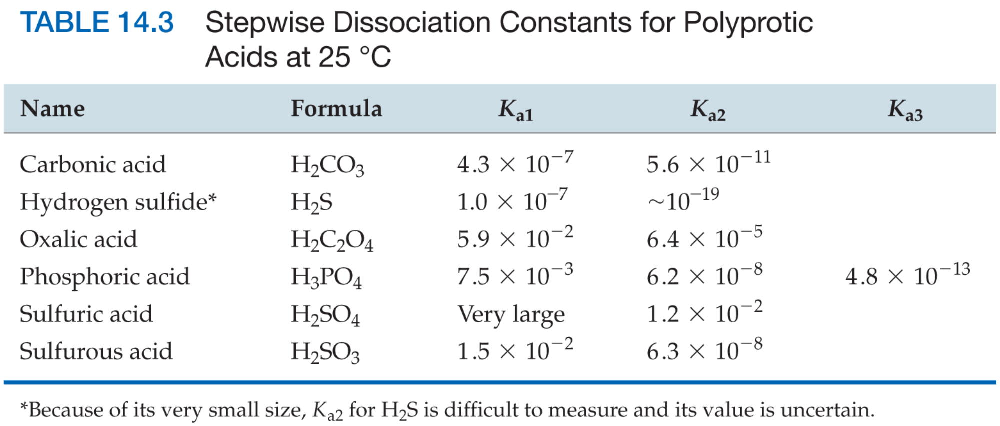


TABLE 14.3 Stepwise Dissociation Constants for Polyprotic Acids at 25 °C

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Hydrogen sulfide*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	6.4×10^{-5}	
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Sulfuric acid	H_2SO_4	Very large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	6.3×10^{-8}	

*Because of its very small size, K_{a2} for H_2S is difficult to measure and its value is uncertain.

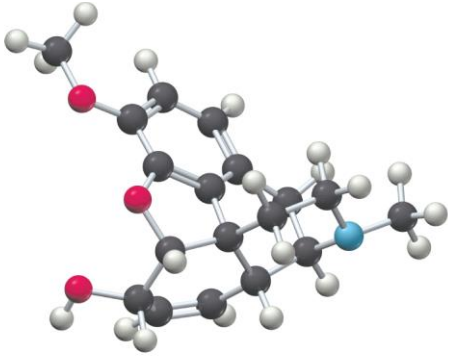
PROBLEM 14.18 Like sulfuric acid, selenic acid (H_2SeO_4) is a diprotic acid that has a very large value of K_{a1}. Calculate the pH and the concentrations of all species present in 0.50 M H_2SeO_4 ($K_{a2} = 1.2 \times 10^{-2}$).

WORKED EXAMPLE 14.13 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Base

Codeine ($C_{18}H_{21}NO_3$), a drug used in painkillers and cough medicines, is a naturally occurring amine that has Kb = 1.6×10^{-6}. Calculate the pH and the concentrations of all species present in a 0.0012 M solution of codeine.

Strategy

Use the procedure outlined in Figure 14.7.



Codeine

Solution

Step 1 Let’s use Cod as an abbreviation for codeine and $CodH^+$ for its conjugate acid. The species present initially are Cod (base) and H_2O (acid or base).

Step 2 There are two possible proton-transfer reactions:

$$Cod(aq) + H_2O(l) \rightleftharpoons CodH^+(aq) + OH^-(aq) \qquad K_b = 1.6 \times 10^{-6}$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = 1.0 \times 10^{-14}$$

Step 3 Since Cod is a much stronger base than H_2O ($K_b \gg K_w$), the principal reaction involves the protonation of codeine.

Step 4

Principal Reaction	$Cod(aq) + H_2O(l) \rightleftharpoons$	$CodH^+(aq) +$	$OH^-(aq)$
Initial concentration (M)	0.0012	0	~0
Change (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$0.0012 - x$	x	x

Step 5 The value of x is obtained from the equilibrium equation:

$$K_b = 1.6 \times 10^{-6} = \frac{[CodH^+][OH^-]}{[Cod]} = \frac{(x)(x)}{(0.0012 - x)}$$

WORKED EXAMPLE 14.13 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Base

Continued

Assuming that $(0.0012 - x) \approx 0.0012$,

$$x^2 = (1.6 \times 10^{-6})(0.0012)$$
$$x = 4.4 \times 10^{-5} \quad \text{Approximation } (0.0012 - x) \approx 0.0012 \text{ is justified.}$$

Step 6 The big concentrations are

$$[\mathrm{CodH^+}] = [\mathrm{OH^-}] = x = 4.4 \times 10^{-5}\ \mathrm{M}$$
$$[\mathrm{Cod}] = 0.0012 - x = 0.0012 - 0.000\,044 = 0.0012\ \mathrm{M}$$

Step 7 The small concentration is obtained from the subsidiary equilibrium, the dissociation of water:

$$[\mathrm{H_3O^+}] = \frac{K_w}{[\mathrm{OH^-}]} = \frac{1.0 \times 10^{-14}}{4.4 \times 10^{-5}} = 2.3 \times 10^{-10}\ \mathrm{M}$$

Step 8 $\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(2.3 \times 10^{-10}) = 9.64$

The pH is greater than 7, as expected for a solution of a weak base.

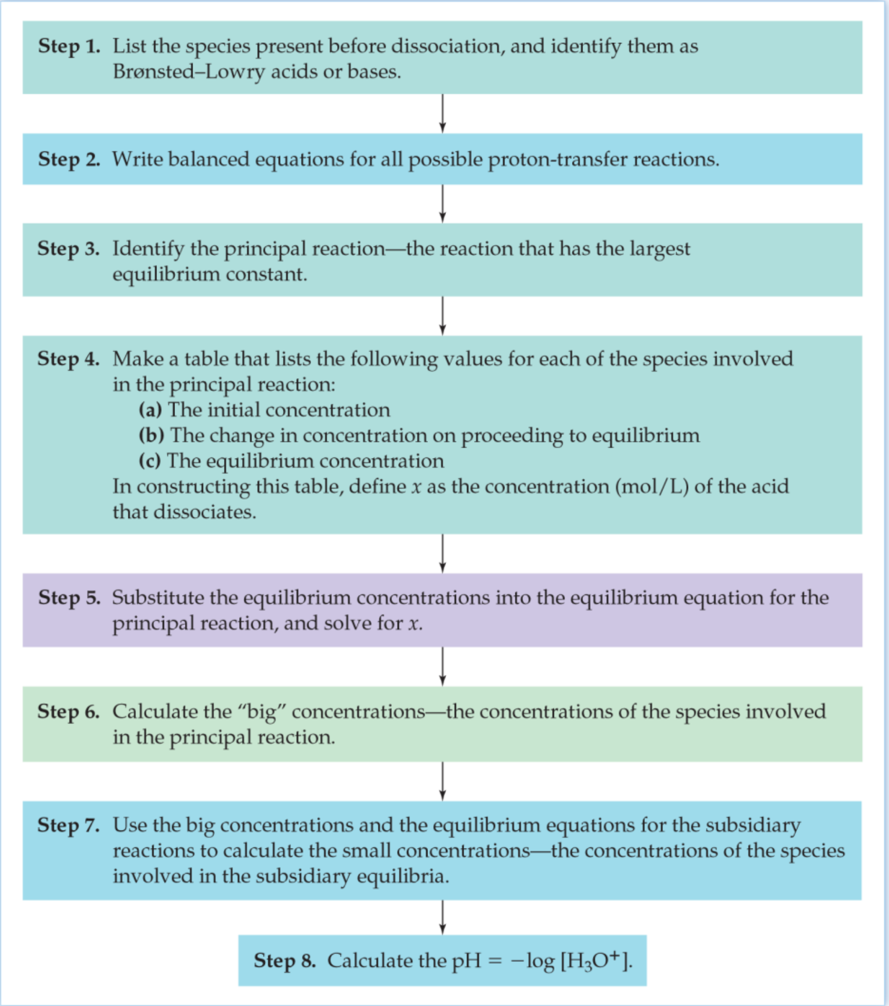
Ballpark Check

Because x is negligible compared with the initial concentration of codeine (Step 5), the $[\mathrm{OH^-}]$ equals the square root of the product of K_b and the initial concentration of codeine. Therefore, $[\mathrm{OH^-}]$ equals the square root of approximately $(16 \times 10^{-7}) \times (1 \times 10^{-3})$, or about 4×10^{-5}. Since the $[\mathrm{OH^-}]$ is between 10^{-5} M and 10^{-4} M, the $[\mathrm{H_3O^+}]$ is between 10^{-9} M and 10^{-10} M, and so the pH is between 9 and 10. The ballpark check and the solution agree.

WORKED EXAMPLE 14.13 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Base

Continued

FIGURE 14.7
Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:
- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the "big" concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

Step 8. Calculate the pH = $-\log [H_3O^+]$.

WORKED EXAMPLE 14.13 Calculating the pH and the Equilibrium Concentrations in a Solution of a Weak Base

Continued

PROBLEM 14.19 Calculate the pH and the concentrations of all species present in 0.40 M NH_3 ($K_b = 1.8 \times 10^{-5}$).

PROBLEM 14.20 Strychnine ($C_{21}H_{22}N_2O_2$), a deadly poison used for killing rodents, is a weak base having $K_b = 1.8 \times 10^{-6}$. Calculate the pH of a saturated solution of strychnine (16 mg/100 mL).

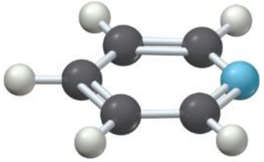
WORKED EXAMPLE 14.14 Relating K_a, K_b, pK_a, and pK_b

(a) K_b for trimethylamine is 6.5×10^{-5}. Calculate K_a for the trimethylammonium ion, $(CH_3)_3NH^+$.

(b) K_a for HCN is 4.9×10^{-10}. Calculate K_b for CN^-.

(c) Pyridine (C_5H_5N), an organic solvent, has pK_b = 8.74. What is the value of pK_a for the pyridinium ion, $C_5H_5NH^+$?

Strategy


Pyridine

To calculate K_a from K_b (or vice versa), use the equation $K_a = K_w/K_b$ or $K_b = K_w/K_a$.
To calculate pK_a from pK_b, use the equation pK_a = 14.00 – pK_b.

Solution

(a) K_a for $(CH_3)_3NH^+$ is the equilibrium constant for the acid-dissociation reaction

$$(CH_3)_3NH^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + (CH_3)_3N(aq)$$

Because $K_a = K_w/K_b$, we can find K_a for $(CH_3)_3NH^+$ from K_b for its conjugate base $(CH_3)_3N$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10}$$

(b) K_b for CN^- is the equilibrium constant for the base-protonation reaction

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$$

Because $K_b = K_w/K_a$, we can find K_b for CN^- from K_a for its conjugate base HCN:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.0 \times 10^{-5}$$

(c) We can find pK_a for $C_5H_5NH^+$ from pK_b for C_5H_5N:

$$pK_a = 14.00 - pK_b = 14.00 - 8.74 = 5.26$$

WORKED EXAMPLE 14.14 Relating K_a, K_b, pK_a, and pK_b

Continued

PROBLEM 14.21

(a) Piperidine ($C_5H_{11}N$) is an amine found in black pepper. Find K_b for piperidine in Appendix C,and then calculate K_a for the $C_5H_{11}NH^+$ cation.

(b) Find K_a for HOCl in Appendix C, and then calculate K_b for OCl^-.

(c) The value of pK_a for formic acid (HCO_2H) is 3.74. What is the value of p$K_b$for the formate ion (HCO_2^-)?

WORKED EXAMPLE 14.15 Calculating the pH of an Acidic Salt Solution

Calculate the pH of a 0.10 M solution of $A1C1_3$; K_a for $A1(H_2O)_6^{3+}$ is 1.4×10^{-5}.

Strategy

Because this problem is similar to others done earlier, we'll abbreviate the procedure in Figure 14.7.

Solution

Step 1–4 The species present initially are $A1(H_2O)_6^{3+}$ (acid), $C1^-$ (inert), and H_2O (acid or base). Because $A1(H_2O)_6^{3+}$ is a much stronger acid than water ($K_a \gg K_w$), the principal reaction is dissociation of $A1(H_2O)_6^{3+}$:

Principal Reaction	$Al(H_2O)_6^{3+}(aq) + H_2O(l) \rightleftharpoons$	$H_3O^+(aq) +$	$Al(H_2O)_5(OH)^{2+}(aq)$
Equilibrium concentration (M)	$0.10 - x$	x	x

Step 5 The value of x is obtained from the equilibrium equation:

$$K_a = 1.4 \times 10^{-5} = \frac{[H_3O^+][Al(H_2O)_5(OH)^{2+}]}{[Al(H_2O)_6^{3+}]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{x^2}{0.10}$$

$$x = [H_3O^+] = 1.2 \times 10^{-3}\,M$$

Step 6 $pH = -\log(1.2 \times 10^{-3}) = 2.92$

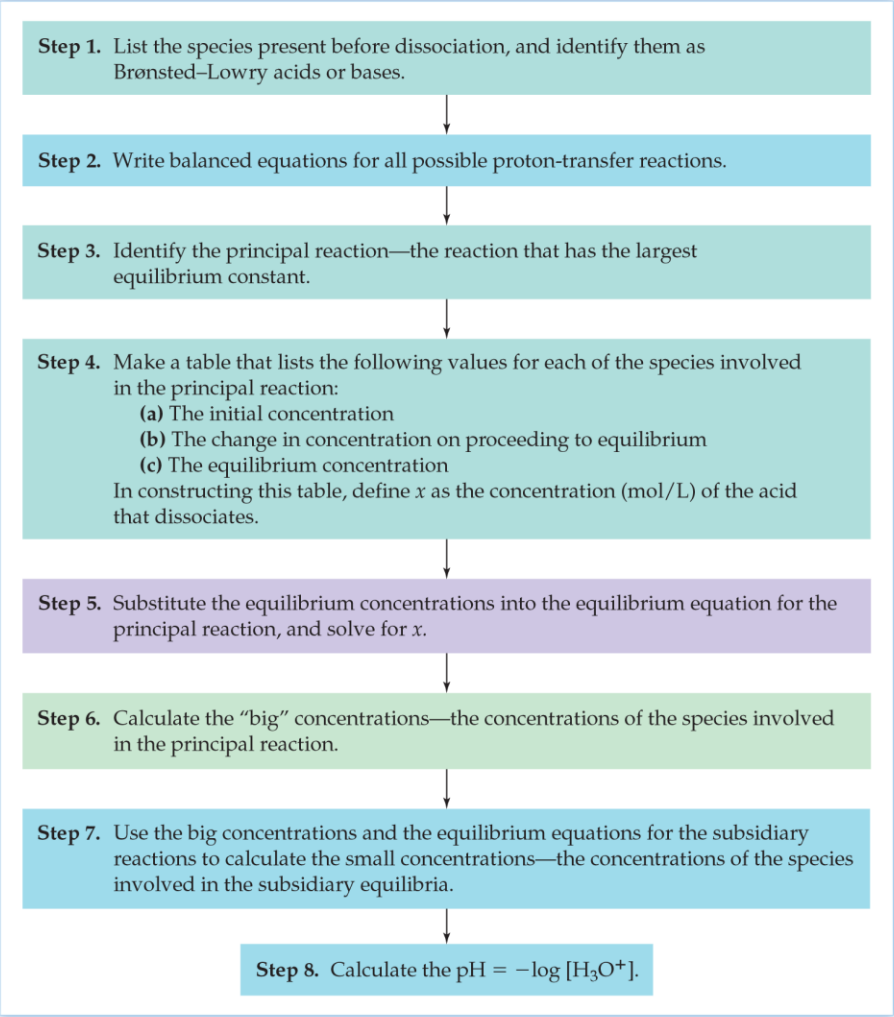
Thus, $A1(H_2O)_6^{3+}$ is a much stronger acid than NH_4^+, which agrees with the colors of the indicator in Figure 14.9.

WORKED EXAMPLE 14.15 Calculating the pH of an Acidic Salt Solution

Continued

FIGURE 14.7

Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:
- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the "big" concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

Step 8. Calculate the pH = $-\log [H_3O^+]$.

WORKED EXAMPLE 14.15 Calculating the pH of an Acidic Salt Solution

Continued

PROBLEM 14.22 Predict whether the following salt solutions are neutral or acidic, and calculate the pH of each:

(a) 0.25 M NH_4Br

(b) 0.40 M $ZnCl_2$; K_a for $Zn(H_2O)_6^{2+}$ is 2.5×10^{-10}.

WORKED EXAMPLE 14.16 Calculating the pH of a Basic Salt Solution

Calculate the pH of a 0.10 M solution of NaCN; K_a for HCN is 4.9×10^{-10}.

Strategy

Use the procedure summarized in Figure 14.7.

Solution

Step 1 The species present initially are Na^+ (inert), CN^- (base), and H_2O (acid or base).

Step 2 There are two possible proton-transfer reactions:

$$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq) \qquad K_b$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w$$

Step 3 As shown in Worked Example 14.14b, $K_b = K_w/(K_a \text{ for HCN}) = 2.0 \times 10^{-5}$. Because $K_b \gg K_w$, CN^- is a stronger base than H_2O and the principal reaction is proton transfer from H_2O to CN^-.

Step 4

Principal Reaction	$CN^-(aq)$ + $H_2O(l)$ ⇌	$HCN(aq)$ +	$OH^-(aq)$
Equilibrium concentration (M)	$0.10 - x$	x	x

Step 5 The value of x is obtained from the equilibrium equation:

$$K_b = 2.0 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]} = \frac{(x)(x)}{(0.10 - x)} \approx \frac{x^2}{0.10}$$

$$x = [OH^-] = 1.4 \times 10^{-3}\ M$$

Step 7 $[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.1 \times 10^{-12}$

Step 8 $pH = -\log(7.1 \times 10^{-12}) = 11.15$

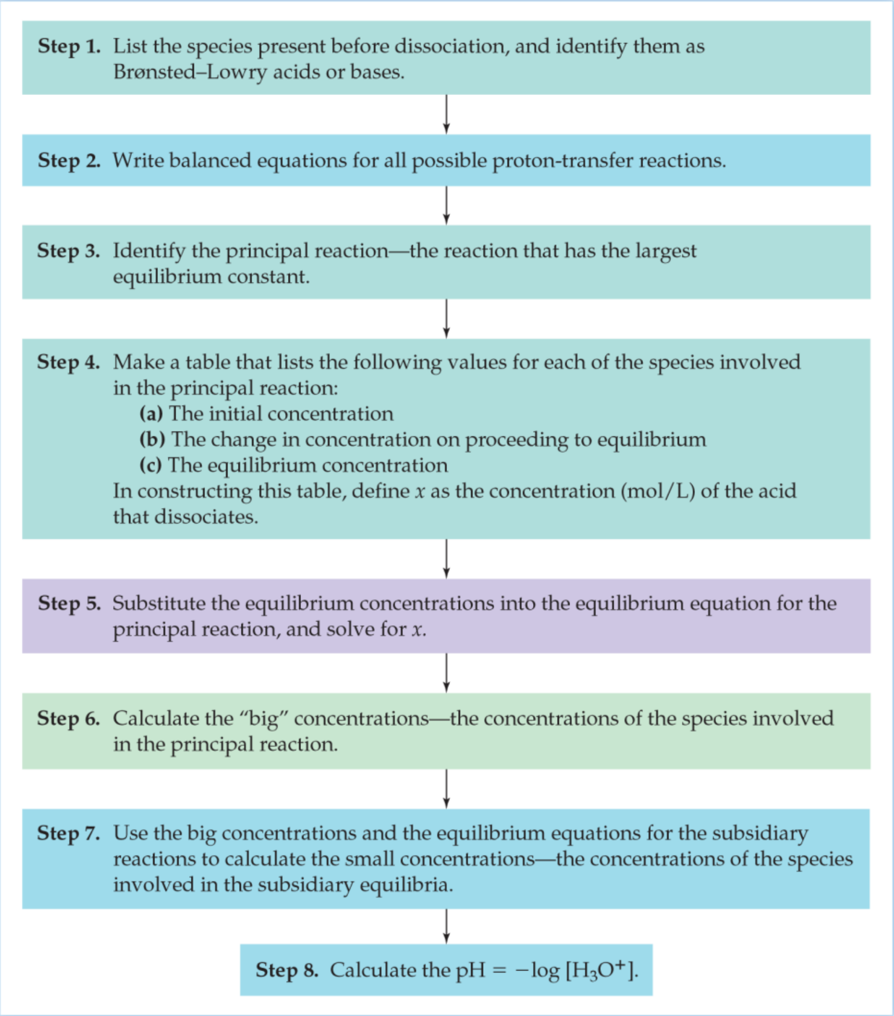
The solution is basic, which agrees with the color of the indicator in Figure 14.9.

WORKED EXAMPLE 14.16 Calculating the pH of a Basic Salt Solution

Continued

FIGURE 14.7

Steps to follow in solving problems involving weak acids.



Step 1. List the species present before dissociation, and identify them as Brønsted–Lowry acids or bases.

Step 2. Write balanced equations for all possible proton-transfer reactions.

Step 3. Identify the principal reaction—the reaction that has the largest equilibrium constant.

Step 4. Make a table that lists the following values for each of the species involved in the principal reaction:

- **(a)** The initial concentration
- **(b)** The change in concentration on proceeding to equilibrium
- **(c)** The equilibrium concentration

In constructing this table, define x as the concentration (mol/L) of the acid that dissociates.

Step 5. Substitute the equilibrium concentrations into the equilibrium equation for the principal reaction, and solve for x.

Step 6. Calculate the “big” concentrations—the concentrations of the species involved in the principal reaction.

Step 7. Use the big concentrations and the equilibrium equations for the subsidiary reactions to calculate the small concentrations—the concentrations of the species involved in the subsidiary equilibria.

Step 8. Calculate the pH = $-\log [H_3O^+]$.

WORKED EXAMPLE 14.16 Calculating the pH of a Basic Salt Solution

Continued

PROBLEM 14.23 Calculate the pH of 0.20 M $NaNO_2$; K_a for HNO_2 is 4.6×10^{-4}.

WORKED EXAMPLE 14.17 Identifying Lewis Acids and Bases

For each of the following reactions, identify the Lewis acid and the Lewis base.

(a) $CO_2 + OH^- \rightarrow HCO_3^-$

(b) $B(OH)_3 + OH^- \rightarrow B(OH)_4^-$

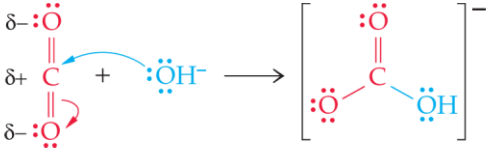
(c) $6\,CN^- + Fe^{3+} \rightarrow Fe(CN)_6^{3-}$

Strategy

To identify the Lewis acid and the Lewis base, determine which molecule or ion can accept an electron pair (the Lewis acid) and which can donate an electron pair (the Lewis base).

Solution

(a) The carbon atom of O=C=O bears a partial positive charge (δ+) because carbon is less electronegative than oxygen. Therefore, the carbon atom attracts an electron pair from OH^-. Formation of a covalent bond from OH^- to CO_2 is helped along by a shift of a shared electron pair to oxygen:
The Lewis acid (electron-pair acceptor) is CO_2; the Lewis base (electron-pair donor) is OH^-.



(b) The Lewis acid is boric acid, $B(OH)_3$, a weak acid and mild antiseptic used in eyewash. The boron atom in $B(OH)_3$ has a vacant valence orbital and completes its octet by accepting a share in a pair of electrons from the Lewis base, OH^-.

(c) The Lewis acid is Fe^{3+}, and the Lewis base is CN^-. Each of the six C≡N:⁻ ions bond to the Fe^{3+} ion by donating a lone pair of electrons on the C atom.

WORKED EXAMPLE 14.17 Identifying Lewis Acids and Bases

Continued

PROBLEM 14.27 For each of the following reactions, identify the Lewis acid and the Lewis base.

(a) $AlCl_3 + Cl^- \rightarrow AlCl_4^-$

(b) $2\,NH_3 + Ag^+ \rightarrow Ag(NH_3)_2^+$

(c) $SO_2 + OH^- \rightarrow HSO_3^-$

(d) $6\,H_2O + Cr^{3+} \rightarrow Cr(H_2O)_6^{3+}$