14.2 35, 36, 37 (39 – 44 ≤ 11)

c. This expression holds true for strong bases that donate 2 OH^- ions per formula unit. As long as the concentration of the base is above 5×10^{-7} *M*, this expression will hold true. Three examples are 5.0×10^{-3} *M* $Ca(OH)_2$, 2.1×10^{-4} *M* $Sr(OH)_2$, and 9.1×10^{-5} *M* $Ba(OH)_2$.

d. This expression holds true for solutions of weak bases where the two normal assumptions hold. The assumptions are that the OH^- contribution from water is negligible and that and that the base is less than 5% ionized in water (for the 5% rule to hold). For the 5% rule to hold, you generally need bases with $K_b < 1 \times 10^{-4}$, and concentrations of weak base greater than 0.10 *M*. Three examples are 0.10 *M* NH_3, 0.54 *M* $C_6H_5NH_2$, and 1.1 *M* C_5H_5N.

33. One reason HF is a weak acid is that the H–F bond is unusually strong and is difficult to break. This contributes significantly to the reluctance of the HF molecules to dissociate in water.

Exercises

Nature of Acids and Bases

35. a. $HClO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + ClO_4^-(aq)$. Only the forward reaction is indicated because $HClO_4$ is a strong acid and is basically 100% dissociated in water. For acids, the dissociation reaction is commonly written without water as a reactant. The common abbreviation for this reaction is $HClO_4(aq) \rightarrow H^+(aq) + ClO_4^-(aq)$. This reaction is also called the K_a reaction because the equilibrium constant for this reaction is designated as K_a.

b. Propanoic acid is a weak acid, so it is only partially dissociated in water. The dissociation reaction is:

$$CH_3CH_2CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CH_2CO_2^-(aq) \quad \text{or}$$

$$CH_3CH_2CO_2H(aq) \rightleftharpoons H^+(aq) + CH_3CH_2CO_2^-(aq).$$

c. NH_4^+ is a weak acid. Similar to propanoic acid, the dissociation reaction is:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq) \quad \text{or} \quad NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$$

37. An acid is a proton (H^+) donor, and a base is a proton acceptor. A conjugate acid-base pair differs by only a proton (H^+).

	Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a.	H_2CO_3	H_2O	HCO_3^-	H_3O^+
b.	$C_5H_5NH^+$	H_2O	C_5H_5N	H_3O^+
c.	$C_5H_5NH^+$	HCO_3^-	C_5H_5N	H_2CO_3

39. Strong acids have a $K_a >> 1$, and weak acids have $K_a < 1$. Table 14.2 in the text lists some K_a values for weak acids. K_a values for strong acids are hard to determine, so they are not listed in the text. However, there are only a few common strong acids so, if you memorize the strong acids, then all other acids will be weak acids. The strong acids to memorize are HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4.

a. $HClO_4$ is a strong acid.

b. HOCl is a weak acid ($K_a = 3.5 \times 10^{-8}$).

c. H_2SO_4 is a strong acid.

d. H_2SO_3 is a weak diprotic acid because the K_{a1} and K_{a2} values are much less than 1.

41. The K_a value is directly related to acid strength. As K_a increases, acid strength increases. For water, use K_w when comparing the acid strength of water to other species. The K_a values are:

$HClO_4$: strong acid ($K_a >> 1$); $HClO_2$: $K_a = 1.2 \times 10^{-2}$

NH_4^+: $K_a = 5.6 \times 10^{-10}$; H_2O: $K_a = K_w = 1.0 \times 10^{-14}$

From the K_a values, the ordering is $HClO_4 > HClO_2 > NH_4^+ > H_2O$.

43. a. HCl is a strong acid, and water is a very weak acid with $K_a = K_w = 1.0 \times 10^{-14}$. HCl is a much stronger acid than H_2O.

b. H_2O, $K_a = K_w = 1.0 \times 10^{-14}$; HNO_2, $K_a = 4.0 \times 10^{-4}$; HNO_2 is a stronger acid than H_2O because K_a for $HNO_2 > K_w$ for H_2O.

c. HOC_6H_5, $K_a = 1.6 \times 10^{-10}$; HCN, $K_a = 6.2 \times 10^{-10}$; HCN is a slightly stronger acid than HOC_6H_5 because K_a for HCN > K_a for HOC_6H_5.

Autoionization of Water and the pH Scale

45. At 25°C, the relationship $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$ always holds for aqueous solutions. When $[H^+]$ is greater than 1.0×10^{-7} *M*, the solution is acidic; when $[H^+]$ is less than 1.0×10^{-7} *M*, the solution is basic; when $[H^+] = 1.0 \times 10^{-7}$ *M*, the solution is neutral. In terms of $[OH^-]$, an acidic solution has $[OH^-] < 1.0 \times 10^{-7}$ *M*, a basic solution has $[OH^-] > 1.0 \times 10^{-7}$ *M*, and a neutral solution has $[OH^-] = 1.0 \times 10^{-7}$ *M*.

a. $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}\ M$; the solution is neutral.

b. $[OH^-] = \frac{1.0 \times 10^{-14}}{8.3 \times 10^{-16}} = 12\ M$; the solution is basic.

36, 40, 42, 44 14.2a

36 a) $HCN \leftrightarrow H^+ + CN^-$

b) $HOC_6H_5 \leftrightarrow H^+ + OC_6H_5^-$

c $C_6H_5NH^+ \leftrightarrow C_6H_5N + H^+$

40 a) Weak → R

b) Strong ← L

c) Strong ← L

d) Weak → R

e) Weak → R

Weak Acid → right further
Strong ← left

42 $NH_3 > ClO_2^- > H_2O > ClO_4^-$ Base Strength

↑ Conj. Base of Strong Acid

Small K_a → Large K_a
Large K_b ← Small K_b

44 Base Strength

a) H_2O

b) NO_2^-

c) $OC_6H_5^-$

$HOC_6H_5 < HCN$ K_a so
$OC_6H_5^- > CN^-$ K_b