

$$K_{a_2} = 1.0 \times 10^{-19} = \frac{(1.0 \times 10^{-4} + x)x}{(1.0 \times 10^{-4} - x)} \approx \frac{(1.0 \times 10^{-4})x}{1.0 \times 10^{-4}}$$

$$x = [S^{2-}] = 1.0 \times 10^{-19} M; \text{ assumptions good.}$$

111. The dominant H^+ producer is the strong acid H_2SO_4 . A 2.0 M H_2SO_4 solution produces 2.0 M HSO_4^- and 2.0 M H^+ . However, HSO_4^- is a weak acid that could also add H^+ to the solution.

	HSO_4^-	\rightleftharpoons	H^+	+	SO_4^{2-}
Initial	2.0 M		2.0 M		0
	x mol/L HSO_4^- dissociates to reach equilibrium				
Change	$-x$	\rightarrow	$+x$		$+x$
Equil.	$2.0 - x$		$2.0 + x$		x

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \frac{(2.0 + x)x}{2.0 - x} \approx \frac{2.0(x)}{2.0}, \quad x = 1.2 \times 10^{-2} M$$

Because x is 0.60% of 2.0, the assumption is valid by the 5% rule. The amount of additional H^+ from HSO_4^- is $1.2 \times 10^{-2} M$. The total amount of H^+ present is:

$$[H^+] = 2.0 + (1.2 \times 10^{-2}) = 2.0 M; \quad pH = -\log(2.0) = -0.30$$

Note: In this problem, H^+ from HSO_4^- could have been ignored. However, this is not usually the case in more dilute solutions of H_2SO_4 .

Acid-Base Properties of Salts

113.

One difficult aspect of acid-base chemistry is recognizing what types of species are present in solution, that is, whether a species is a strong acid, strong base, weak acid, weak base, or a neutral species. Below are some ideas and generalizations to keep in mind that will help in recognizing types of species present.

- a. Memorize the following strong acids: HCl, HBr, HI, HNO_3 , $HClO_4$, and H_2SO_4
- b. Memorize the following strong bases: LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$
- c. Weak acids have a K_a value of less than 1 but greater than K_w . Some weak acids are listed in Table 14.2 of the text. Weak bases have a K_b value of less than 1 but greater than K_w . Some weak bases are listed in Table 14.3 of the text.
- d. Conjugate bases of weak acids are weak bases; that is, all have a K_b value of less than 1 but greater than K_w . Some examples of these are the conjugate bases of the weak acids listed in Table 14.2 of the text.
- e. Conjugate acids of weak bases are weak acids; that is, all have a K_a value of less than 1 but greater than K_w . Some examples of these are the conjugate acids of the weak bases listed in Table 14.3 of the text.

- (113)
- f. Alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and heavier alkaline earth metal ions (Ca^{2+} , Sr^{2+} , Ba^{2+}) have no acidic or basic properties in water.
- g. All conjugate bases of strong acids (Cl^- , Br^- , I^- , NO_3^- , ClO_4^- , HSO_4^-) have no basic properties in water ($K_b \ll K_w$), and only HSO_4^- has any acidic properties in water.

Let's apply these ideas to this problem to see what type of species are present. The letters in parenthesis is(are) the generalization(s) above that identifies the species.

KOH: Strong base (b)

KNO_3 : Neutral; K^+ and NO_3^- have no acidic/basic properties (f and g).

KCN: CN^- is a weak base, $K_b = K_w/K_{a,\text{HCN}} = 1.0 \times 10^{-14}/6.2 \times 10^{-10} = 1.6 \times 10^{-5}$ (c and d). Ignore K^+ (f).

NH_4Cl : NH_4^+ is a weak acid, $K_a = 5.6 \times 10^{-10}$ (c and e). Ignore Cl^- (g).

HCl: Strong acid (a)

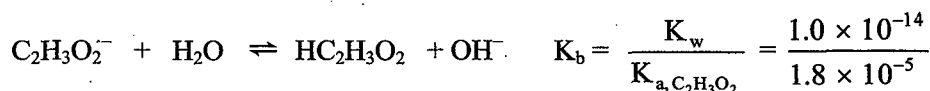
The most acidic solution will be the strong acid solution, with the weak acid solution less acidic. The most basic solution will be the strong base solution, with the weak base solution less basic. The KNO_3 solution will be neutral at $\text{pH} = 7.00$.

Most acidic \rightarrow most basic: $\text{HCl} > \text{NH}_4\text{Cl} > \text{KNO}_3 > \text{KCN} > \text{KOH}$

(115.) From the K_a values, acetic acid is a stronger acid than hypochlorous acid. Conversely, the conjugate base of acetic acid, $\text{C}_2\text{H}_3\text{O}_2^-$, will be a weaker base than the conjugate base of hypochlorous acid, OCl^- . Thus the hypochlorite ion, OCl^- , is a stronger base than the acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-$. In general, the stronger the acid, the weaker the conjugate base. This statement comes from the relationship $K_w = K_a \times K_b$, which holds for all conjugate acid-base pairs.

- (117.)
- a. KCl is a soluble ionic compound that dissolves in water to produce $\text{K}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$. K^+ (like the other alkali metal cations) has no acidic or basic properties. Cl^- is the conjugate base of the strong acid HCl. Cl^- has no basic (or acidic) properties. Therefore, a solution of KCl will be neutral because neither of the ions has any acidic or basic properties. The 1.0 M KCl solution has $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$ and $\text{pH} = \text{pOH} = 7.00$.
- b. $\text{KC}_2\text{H}_3\text{O}_2$ is also a soluble ionic compound that dissolves in water to produce $\text{K}^+(\text{aq})$ and $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$. The difference between the KCl solution and the $\text{KC}_2\text{H}_3\text{O}_2$ solution is that $\text{C}_2\text{H}_3\text{O}_2^-$ does have basic properties in water, unlike Cl^- . $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base of the weak acid $\text{HC}_2\text{H}_3\text{O}_2$, and as is true for all conjugate bases of weak acids, $\text{C}_2\text{H}_3\text{O}_2^-$ is a weak base in water. We must solve an equilibrium problem in order to determine the amount of OH^- this weak base produces in water.

117



Initial 1.0 M 0 ~0 $K_b = 5.6 \times 10^{-10}$
 x mol/L of $\text{C}_2\text{H}_3\text{O}_2^-$ reacts with H_2O to reach equilibrium

Change $-x$ \rightarrow $+x$ $+x$

Equil. 1.0 - x x x

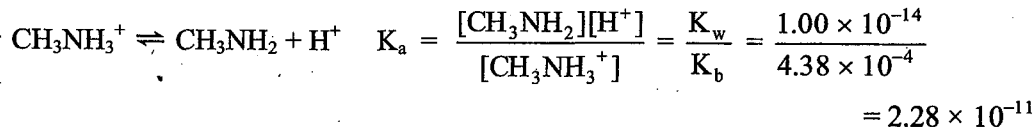
$$K_b = 5.6 \times 10^{-10} = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]}, \quad 5.6 \times 10^{-10} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$x = [\text{OH}^-] = 2.4 \times 10^{-5} \text{ M}$; assumptions good

pOH = 4.62; pH = 14.00 - 4.62 = 9.38; $[\text{H}^+] = 10^{-9.38} = 4.2 \times 10^{-10} \text{ M}$

119.

- a. $\text{CH}_3\text{NH}_3\text{Cl} \rightarrow \text{CH}_3\text{NH}_3^+ + \text{Cl}^-$: CH_3NH_3^+ is a weak acid. Cl^- is the conjugate base of a strong acid. Cl^- has no basic (or acidic) properties.



Initial 0.10 M 0 ~0
 x mol/L CH_3NH_3^+ dissociates to reach equilibrium

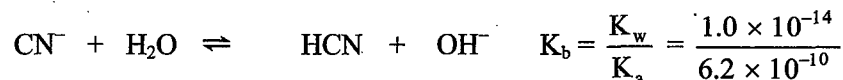
Change $-x$ \rightarrow $+x$ $+x$

Equil. 0.10 - x x x

$$K_a = 2.28 \times 10^{-11} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10} \quad (\text{assuming } x \ll 0.10)$$

$x = [\text{H}^+] = 1.5 \times 10^{-6} \text{ M}$; pH = 5.82; assumptions good.

- b. $\text{NaCN} \rightarrow \text{Na}^+ + \text{CN}^-$: CN^- is a weak base. Na^+ has no acidic (or basic) properties.



Initial 0.050 M 0 ~0 $K_b = 1.6 \times 10^{-5}$
 x mol/L CN^- reacts with H_2O to reach equilibrium

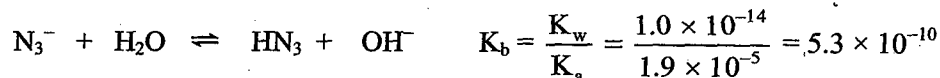
Change $-x$ \rightarrow $+x$ $+x$

Equil. 0.050 - x x x

$$K_b = 1.6 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = [\text{OH}^-] = 8.9 \times 10^{-4} \text{ M}$; pOH = 3.05; pH = 10.95; assumptions good.

121. $\text{NaN}_3 \rightarrow \text{Na}^+ + \text{N}_3^-$; azide (N_3^-) is a weak base because it is the conjugate base of a weak acid. All conjugate bases of weak acids are weak bases ($K_w < K_b < 1$). Ignore Na^+ .



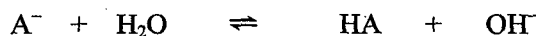
Initial	0.010 M	0	~0
	x mol/L of N_3^- reacts with H_2O to reach equilibrium		
Change	-x	+x	+x
Equil.	0.010 - x	x	x

$$K_b = \frac{[\text{HN}_3][\text{OH}^-]}{[\text{N}_3^-]}, \quad 5.3 \times 10^{-10} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010} \quad (\text{assuming } x \ll 0.010)$$

$$x = [\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}; \quad [\text{H}^+] = \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-6}} = 4.3 \times 10^{-9} \text{ M}; \quad \text{assumptions good.}$$

$$[\text{HN}_3] = [\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}; \quad [\text{Na}^+] = 0.010 \text{ M}; \quad [\text{N}_3^-] = 0.010 - 2.3 \times 10^{-6} = 0.010 \text{ M}$$

123. All these salts contain Na^+ , which has no acidic/basic properties, and a conjugate base of a weak acid (except for NaCl , where Cl^- is a neutral species). All conjugate bases of weak acids are weak bases since K_b values for these species are between K_w and 1. To identify the species, we will use the data given to determine the K_b value for the weak conjugate base. From the K_b value and data in Table 14.2 of the text, we can identify the conjugate base present by calculating the K_a value for the weak acid. We will use A^- as an abbreviation for the weak conjugate base.



Initial	0.100 mol/1.00 L	0	~0
	x mol/L A^- reacts with H_2O to reach equilibrium		
Change	-x	+x	+x
Equil.	0.100 - x	x	x

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x^2}{0.100 - x}; \quad \text{from the problem, pH} = 8.07:$$

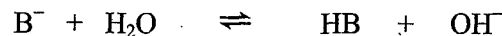
$$\text{pOH} = 14.00 - 8.07 = 5.93; \quad [\text{OH}^-] = x = 10^{-5.93} = 1.2 \times 10^{-6} \text{ M}$$

$$K_b = \frac{(1.2 \times 10^{-6})^2}{0.100 - (1.2 \times 10^{-6})} = 1.4 \times 10^{-11} = K_b \text{ value for the conjugate base of a weak acid.}$$

$$\text{The } K_a \text{ value for the weak acid equals } K_w/K_b: \quad K_a = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-11}} = 7.1 \times 10^{-4}$$

From Table 14.2 of the text, this K_a value is closest to HF. Therefore, the unknown salt is NaF.

125. B^- is a weak base. Use the weak base data to determine K_b for B^- .



Initial	0.050 M	0	~0
Equil.	0.050 - x	x	x

From pH = 9.00: pOH = 5.00, $[OH^-] = 10^{-5.00} = 1.0 \times 10^{-5} M = x$.

$$K_b = \frac{[HB][OH^-]}{[B^-]} = \frac{x^2}{0.050 - x} = \frac{(1.0 \times 10^{-5})^2}{0.050 - (1.0 \times 10^{-5})} = 2.0 \times 10^{-9}$$

Because B^- is a weak base, HB will be a weak acid. Solve the weak acid problem.

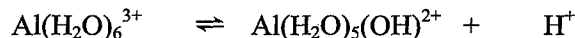


Initial	0.010 M	~0	0
Equil.	0.010 - x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-9}}, \quad 5.0 \times 10^{-6} = \frac{x^2}{0.010 - x} \approx \frac{x^2}{0.010}$$

$x = [H^+] = 2.2 \times 10^{-4} M$; pH = 3.66; assumptions good.

127. Major species present: $Al(H_2O)_6^{3+}$ ($K_a = 1.4 \times 10^{-5}$), NO_3^- (neutral), and H_2O ($K_w = 1.0 \times 10^{-14}$); $Al(H_2O)_6^{3+}$ is a stronger acid than water, so it will be the dominant H^+ producer.



Initial	0.050 M	0	~0
	x mol/L $Al(H_2O)_6^{3+}$ dissociates to reach equilibrium		
Change	-x	+x	+x
Equil.	0.050 - x	x	x

$$K_a = 1.4 \times 10^{-5} = \frac{[Al(H_2O)_5(OH)^{2+}][H^+]}{[Al(H_2O)_6^{3+}]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$x = 8.4 \times 10^{-4} M = [H^+]$; pH = $-\log(8.4 \times 10^{-4}) = 3.08$; assumptions good.

129. Reference Table 14.6 of the text and the solution to Exercise 113 for some generalizations on acid-base properties of salts.

a. $NaNO_3 \rightarrow Na^+ + NO_3^-$ neutral; neither species has any acidic/basic properties.

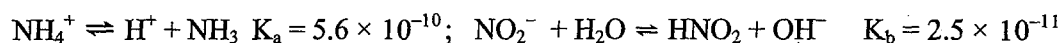
b. $NaNO_2 \rightarrow Na^+ + NO_2^-$ basic; NO_2^- is a weak base, and Na^+ has no effect on pH.

$$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^- \quad K_b = \frac{K_w}{K_{a,HNO_2}} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11}$$

- c. $C_5H_5NHCIO_4 \rightarrow C_5H_5NH^+ + CIO_4^-$ acidic; $C_5H_5NH^+$ is a weak acid, and CIO_4^- has no effect on pH.

$$C_5H_5NH^+ \rightleftharpoons H^+ + C_5H_5N \quad K_a = \frac{K_w}{K_{b,C_5H_5N}} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

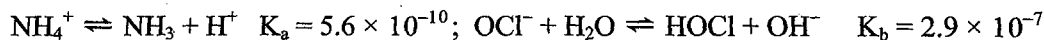
- d. $NH_4NO_2 \rightarrow NH_4^+ + NO_2^-$ acidic; NH_4^+ is a weak acid ($K_a = 5.6 \times 10^{-10}$), and NO_2^- is a weak base ($K_b = 2.5 \times 10^{-11}$). Because $K_{a,NH_4^+} > K_{b,NO_2^-}$, the solution is acidic.



- e. $KOCl \rightarrow K^+ + OCl^-$ basic; OCl^- is a weak base, and K^+ has no effect on pH.

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^- \quad K_b = \frac{K_w}{K_{a,HOCl}} = \frac{1.0 \times 10^{-14}}{3.5 \times 10^{-8}} = 2.9 \times 10^{-7}$$

- f. $NH_4OCl \rightarrow NH_4^+ + OCl^-$ basic; NH_4^+ is a weak acid, and OCl^- is a weak base. Because $K_{b,OCl^-} > K_{a,NH_4^+}$, the solution is basic.



Relationships Between Structure and Strengths of Acids and Bases

131. a. $HIO_3 < HBrO_3$; as the electronegativity of the central atom increases, acid strength increases.
- b. $HNO_2 < HNO_3$; as the number of oxygen atoms attached to the central nitrogen atom increases, acid strength increases.
- c. $HOI < HOCl$; same reasoning as in a.
- d. $H_3PO_3 < H_3PO_4$; same reasoning as in b.
133. a. $H_2O < H_2S < H_2Se$; as the strength of the H–X bond decreases, acid strength increases.
- b. $CH_3CO_2H < FCH_2CO_2H < F_2CHCO_2H < F_3CCO_2H$; as the electronegativity of neighboring atoms increases, acid strength increases.
- c. $NH_4^+ < HONH_3^+$; same reason as in b.
- d. $NH_4^+ < PH_4^+$; same reason as in a.
135. In general, metal oxides form basic solutions when dissolved in water, and nonmetal oxides form acidic solutions in water.
- a. Basic; $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$; $Ca(OH)_2$ is a strong base.
- b. Acidic; $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$; H_2SO_3 is a weak diprotic acid.
- c. Acidic; $Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$; $HOCl$ is a weak acid.