

20.  $K_a \times K_b = K_w$ ,  $-\log(K_a \times K_b) = -\log K_w$

$-\log K_a - \log K_b = -\log K_w$ ,  $pK_a + pK_b = pK_w = 14.00$  (at 25°C)

24.  $H_2CO_3$  is a weak acid with  $K_{a_1} = 4.3 \times 10^{-7}$  and  $K_{a_2} = 5.6 \times 10^{-11}$ . The  $[H^+]$  concentration in solution will be determined from the  $K_{a_1}$  reaction since  $K_{a_1} \gg K_{a_2}$ . Since  $K_{a_1} \ll 1$ , then the  $[H^+] < 0.10 M$ ; only a small percentage of  $H_2CO_3$  will dissociate into  $HCO_3^-$  and  $H^+$ . So statement a best describes the 0.10 M  $H_2CO_3$  solution.  $H_2SO_4$  is a strong acid and a very good weak acid ( $K_{a_1} \gg 1$ ,  $K_{a_2} = 1.2 \times 10^{-2}$ ). All of the 0.1 M  $H_2SO_4$  solution will dissociate into 0.10 M  $H^+$  and 0.10 M  $HSO_4^-$ . However, since  $HSO_4^-$  is a good weak acid due to the relatively large  $K_a$  value, then some of the 0.10 M  $HSO_4^-$  will dissociate into some more  $H^+$  and  $SO_4^{2-}$ . Therefore, the  $[H^+]$  will be greater than 0.10 M, but will not reach 0.20 since only some of 0.10 M  $HSO_4^-$  will dissociate. Statement c is best for a 0.10 M  $H_2SO_4$  solution.

30.

	Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a.	$Al(H_2O)_6^{3+}$	$H_2O$	$Al(H_2O)_5(OH)^{2+}$	$H_3O^+$
b.	$HONH_3^+$	$H_2O$	$HONH_2$	$H_3O^+$
c.	$HOCl$	$C_6H_5NH_2$	$OCl^-$	$C_6H_5NH_3^+$

44. a.  $pOH = 14.00 - 9.63 = 4.37$ ;  $[H^+] = 10^{-9.63} = 2.3 \times 10^{-10} M$

$[OH^-] = 10^{-4.37} = 4.3 \times 10^{-5} M$ ; basic

b.  $[H^+] = \frac{1.0 \times 10^{-14}}{3.9 \times 10^{-6}} = 2.6 \times 10^{-9} M$ ;  $pH = -\log(2.6 \times 10^{-9}) = 8.59$

$pOH = 14.00 - 8.59 = 5.41$ ; basic

c.  $pH = -\log(0.027) = 1.57$ ;  $pOH = 14.00 - 1.57 = 12.43$

$[OH^-] = 10^{-12.43} = 3.7 \times 10^{-13} M$ ; acidic

d.  $pH = 14.0 - 12.2 = 1.8$ ;  $[H^+] = 10^{-1.8} = 2 \times 10^{-2} M$

$[OH^-] = 10^{-12.2} = 6 \times 10^{-13} M$ ; acidic

50.  $90.0 \times 10^{-3} L \times \frac{5.00 \text{ mol}}{L} = 0.450 \text{ mol } H^+ \text{ from HCl}$

$30.0 \times 10^{-3} L \times \frac{8.00 \text{ mol}}{L} = 0.240 \text{ mol } H^+ \text{ from HNO}_3$

$$[\text{H}^+] = \frac{0.450 \text{ mol} + 0.240 \text{ mol}}{1.00 \text{ L}} = 0.690 \text{ M}; \text{ pH} = -\log(0.690) = 0.161$$

$$\text{pOH} = 14.000 - 0.161 = 13.839; [\text{OH}^-] = 10^{-13.839} = 1.45 \times 10^{-14} \text{ M}$$

54. a.  $\text{HOC}_6\text{H}_5$  ( $K_a = 1.6 \times 10^{-10}$ ) and  $\text{H}_2\text{O}$  ( $K_a = K_w = 1.0 \times 10^{-14}$ ) are the major species. The major equilibrium is the dissociation of  $\text{HOC}_6\text{H}_5$ . Solving the weak acid problem:



Initial       $0.250 \text{ M}$                $\sim 0$                $0$   
 $x \text{ mol/L HOC}_6\text{H}_5$  dissociates to reach equilibrium

Change       $-x$                $+x$                $+x$

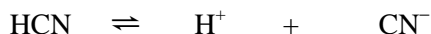
Equil.       $0.250 - x$                $x$                $x$

$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OC}_6\text{H}_5^-]}{[\text{HOC}_6\text{H}_5]} = \frac{x^2}{0.250 - x} \cdot \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

$x = [\text{H}^+] = 6.3 \times 10^{-6} \text{ M}$ ; Checking assumption:  $x$  is  $2.5 \times 10^{-3}\%$  of  $0.250$ , so assumption is valid by the 5% rule.

$$\text{pH} = -\log(6.3 \times 10^{-6}) = 5.20$$

- b.  $\text{HCN}$  ( $K_a = 6.2 \times 10^{-10}$ ) and  $\text{H}_2\text{O}$  are the major species.  $\text{HCN}$  is the major source of  $\text{H}^+$ .



Initial       $0.250 \text{ M}$                $\sim 0$                $0$   
 $x \text{ mol/L HCN}$  dissociates to reach equilibrium

Change       $-x$                $+x$                $+x$

Equil.       $0.250 - x$                $x$                $x$

$$K_a = 6.2 \times 10^{-10} = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{x^2}{0.250 - x} \cdot \frac{x^2}{0.250} \quad (\text{assuming } x \ll 0.250)$$

$x = [\text{H}^+] = 1.2 \times 10^{-5} \text{ M}$ ; Checking assumption:  $x$  is  $4.8 \times 10^{-3}\%$  of  $0.250$

Assumptions good.  $\text{pH} = -\log(1.2 \times 10^{-5}) = 4.92$

$$60. \quad [\text{HC}_9\text{H}_7\text{O}_4] = \frac{2 \text{ tablets} \times \frac{0.325 \text{ g HC}_9\text{H}_7\text{O}_4}{\text{tablet}} \times \frac{1 \text{ mol HC}_9\text{H}_7\text{O}_4}{180.15 \text{ g}}}{0.237 \text{ L}} = 0.0152 \text{ M}$$



Initial	0.0152 M	~0	0
	$x$ mol/L $\text{HC}_9\text{H}_7\text{O}_4$ dissociates to reach equilibrium		
Change	$-x$	$+x$	$+x$
Equil.	$0.0152 - x$	$x$	$x$

$$K_a = 3.3 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_4^-]}{[\text{HC}_9\text{H}_7\text{O}_4]} = \frac{x^2}{0.0152 - x} \approx \frac{x^2}{0.0152}, \quad x = 2.2 \times 10^{-3} \text{ M}$$

Assumption that  $0.0152 - x \approx 0.0152$  fails the 5% rule:  $\frac{2.2 \times 10^{-3}}{0.0152} \times 100 = 14\%$

Using successive approximations or the quadratic equation gives an exact answer of  $x = 2.1 \times 10^{-3} \text{ M}$ .

$$[\text{H}^+] = x = 2.1 \times 10^{-3} \text{ M}; \quad \text{pH} = -\log(2.1 \times 10^{-3}) = 2.68$$

76. a.  $\text{HClO}_4$     b.  $\text{C}_6\text{H}_5\text{NH}_3^+$     c.  $\text{C}_6\text{H}_5\text{NH}_3^+$

The acid with the largest  $K_a$  value is the strongest acid. To calculate  $K_a$  values for  $\text{C}_6\text{H}_5\text{NH}_3^+$  and  $\text{CH}_3\text{NH}_3^+$ , use  $K_a = K_w/K_b$  where  $K_b$  refers to the bases  $\text{C}_6\text{H}_5\text{NH}_2$  or  $\text{CH}_3\text{NH}_2$ .

84. Major species:  $\text{H}_2\text{NNH}_2$  ( $K_b = 3.0 \times 10^{-6}$ ) and  $\text{H}_2\text{O}$  ( $K_b = K_w = 1.0 \times 10^{-14}$ ); The weak base  $\text{H}_2\text{NNH}_2$  will dominate  $\text{OH}^-$  production. We must perform a weak base equilibrium calculation.



Initial	2.0 M	0	~0
	$x$ mol/L $\text{H}_2\text{NNH}_2$ reacts with $\text{H}_2\text{O}$ to reach equilibrium		
Change	$-x$	$+x$	$+x$
Equil.	$2.0 - x$	$x$	$x$

$$K_b = 3.0 \times 10^{-6} = \frac{[\text{H}_2\text{NNH}_3^+][\text{OH}^-]}{[\text{H}_2\text{NNH}_2]} = \frac{x^2}{2.0 - x} \approx \frac{x^2}{2.0} \quad (\text{assuming } x \ll 2.0)$$

$$x = [\text{OH}^-] = 2.4 \times 10^{-3} \text{ M}; \quad \text{pOH} = 2.62; \quad \text{pH} = 11.38 \quad \text{Assumptions good } (x \text{ is } 0.12\% \text{ of } 2.0).$$

$$[\text{H}_2\text{NNH}_3^+] = 2.4 \times 10^{-3} \text{ M}; \quad [\text{H}_2\text{NNH}_2] = 2.0 \text{ M}; \quad [\text{H}^+] = 10^{-11.38} = 4.2 \times 10^{-12} \text{ M}$$

100. See Exercise 14.99 for some generalizations on acid-base properties of salts. The letters in parenthesis is/are the generalization(s) listed in Exercise 14.99 which identifies the species.

CaBr<sub>2</sub>: neutral; Ca<sup>2+</sup> and Br<sup>-</sup> have no acidic/basic properties (f and g).  
 KNO<sub>2</sub>: NO<sub>2</sub><sup>-</sup> is a weak base,  $K_b = 1.0 \times 10^{-14} / 4.0 \times 10^{-4} = 2.5 \times 10^{-11}$  (c and d).  
 Ignore K<sup>+</sup> (f).  
 HClO<sub>4</sub>: strong acid (a)  
 HNO<sub>2</sub>: weak acid,  $K_a = 4.0 \times 10^{-4}$  (c)  
 HONH<sub>3</sub>ClO<sub>4</sub>: HONH<sub>3</sub><sup>+</sup> is a weak acid,  $K_a = 1.0 \times 10^{-14} / 1.1 \times 10^{-8} = 9.1 \times 10^{-7}$  (c and e).  
 Ignore ClO<sub>4</sub><sup>-</sup> (g). Note that HNO<sub>2</sub> has a larger  $K_a$  value than HONH<sub>3</sub><sup>+</sup>, so HNO<sub>2</sub> is a stronger weak acid than HONH<sub>3</sub><sup>+</sup>.

Using the information above (identity and  $K_a$  or  $K_b$  values), the ordering is:

most acidic → most basic: HClO<sub>4</sub> > HNO<sub>2</sub> > HONH<sub>3</sub>ClO<sub>4</sub> > CaBr<sub>2</sub> > KNO<sub>2</sub>

125. At pH = 2.000,  $[H^+] = 10^{-2.000} = 1.00 \times 10^{-2} M$ ; At pH = 4.000,  $[H^+] = 10^{-4.000} = 1.00 \times 10^{-4} M$

$$\text{mol } H^+ \text{ present} = 0.0100 \text{ L} \times \frac{0.0100 \text{ mol } H^+}{\text{L}} = 1.00 \times 10^{-4} \text{ mol } H^+$$

Let V = total volume of solution at pH = 4.000:

$$1.00 \times 10^{-4} \text{ mol/L} = \frac{1.00 \times 10^{-4} \text{ mol } H^+}{V}, \quad V = 1.00 \text{ L}$$

Volume of water added = 1.00 L - 0.0100 L = 0.99 L = 990 mL

136. From the pH, C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub><sup>-</sup> is a weak base. Use the weak base data to determine  $K_b$  for C<sub>7</sub>H<sub>4</sub>ClO<sub>2</sub><sup>-</sup> (which we will abbreviate as CB<sup>-</sup>).

	CB <sup>-</sup>	+	H <sub>2</sub> O	⇌	HCB	+	OH <sup>-</sup>
Initial	0.20 M				0		~0
Equil.	0.20 - x				x		x

Because pH = 8.65, pOH = 5.35 and  $[OH^-] = 10^{-5.35} = 4.5 \times 10^{-6} M = x$ .

$$K_b = \frac{[HCB][OH^-]}{[CB^-]} = \frac{x^2}{0.20 - x} = \frac{(4.5 \times 10^{-6})^2}{0.20 - 4.5 \times 10^{-6}} = 1.0 \times 10^{-10}$$

Since CB<sup>-</sup> is a weak base, HCB, chlorobenzoic acid, is a weak acid. Solving the weak acid problem:

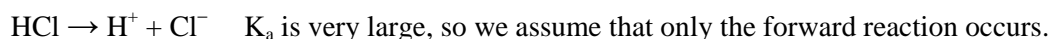
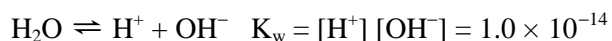


Initial	0.20 M	~0	0
Equil.	0.20 - x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-10}} = 1.0 \times 10^{-4} = \frac{x^2}{0.20 - x} \approx \frac{x^2}{0.20}$$

$$x = [H^+] = 4.5 \times 10^{-3} M; \text{ pH} = 2.35 \quad \text{Assumptions good.}$$

144. The pH of this solution is not 8.00 because water will donate a significant amount of  $H^+$  from the autoionization of water. You can't add an acid to water and get a basic pH. The pertinent reactions are:



In any solution, the overall net positive charge must equal the overall net negative charge (called the charge balance). For this problem:

$$[\text{positive charge}] = [\text{negative charge}], \text{ so } [H^+] = [OH^-] + [Cl^-]$$

From  $K_w$ ,  $[OH^-] = K_w/[H^+]$ , and from  $1.0 \times 10^{-8} M$  HCl,  $[Cl^-] = 1.0 \times 10^{-8} M$ . Substituting into the charge balance equation:

$$[H^+] = \frac{1.0 \times 10^{-14}}{[H^+]} + 1.0 \times 10^{-8}, \quad [H^+]^2 - 1.0 \times 10^{-8} [H^+] + 1.0 \times 10^{-14} = 0$$

Using the quadratic formula to solve:

$$[H^+] = \frac{-(-1.0 \times 10^{-8}) \pm [(-1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})]^{1/2}}{2(1)}, \quad [H^+] = 1.1 \times 10^{-7} M$$

$$\text{pH} = -\log(1.1 \times 10^{-7}) = 6.96$$

$$161. \quad [\text{IO}^-] = \frac{2.14 \text{ g NaIO} \times \frac{1 \text{ mol NaIO}}{165.89 \text{ g}} \times \frac{1 \text{ mol IO}^-}{\text{mol NaIO}}}{1.25 \text{ L}} = 1.03 \times 10^{-2} M \text{ IO}^-$$



$$\frac{[\text{HIO}][\text{OH}^-]}{[\text{IO}^-]}$$

Initial	$1.03 \times 10^{-2} M$	0	$\sim 0$
Equil.	$1.03 \times 10^{-2} - x$	$x$	$x$

$$K_b = \frac{x^2}{1.03 \times 10^{-2} - x}; \quad \text{From the problem, } \text{pOH} = 14.00 - 11.32 = 2.68$$

$$[\text{OH}^-] = 10^{-2.68} = 2.1 \times 10^{-3} M = x; \quad K_b = \frac{(2.1 \times 10^{-3})^2}{1.03 \times 10^{-2} - 2.1 \times 10^{-3}} = 5.4 \times 10^{-4}$$