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Polyprotic Acids

105. $H_2SO_3(aq) \rightleftharpoons HSO_3^-(aq) + H^+(aq)$ $\qquad K_{a_1} = \dfrac{[HSO_3^-][H^+]}{[H_2SO_3]}$

$HSO_3^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H^+(aq)$ $\qquad K_{a_2} = \dfrac{[SO_3^{2-}][H^+]}{[HSO_3^-]}$

107. For $H_2C_6H_6O_6$. $K_{a_1} = 7.9 \times 10^{-5}$ and $K_{a_2} = 1.6 \times 10^{-12}$. Because $K_{a_1} >> K_{a_2}$, the amount of H^+ produced by the K_{a_2} reaction will be negligible.

$$[H_2C_6H_6O_6]_0 = \frac{0.500\text{ g} \times \dfrac{1\text{ mol } H_2C_6H_6O_6}{176.12\text{ g}}}{0.2000\text{ L}} = 0.0142\ M$$

$$H_2C_6H_6O_6(aq) \rightleftharpoons HC_6H_6O_6^-(aq) + H^+(aq) \qquad K_{a_1} = 7.9 \times 10^{-5}$$

Initial	0.0142 *M*	0	~0
Equil.	$0.0142 - x$	x	x

$$K_{a_1} = 7.9 \times 10^{-5} = \frac{x^2}{0.0142 - x} \approx \frac{x^2}{0.0142},\ x = 1.1 \times 10^{-3};\ \text{assumption fails the 5\% rule.}$$

Solving by the method of successive approximations:

$$7.9 \times 10^{-5} = \frac{x^2}{0.0142 - 1.1 \times 10^{-3}},\ x = 1.0 \times 10^{-3}\ M\ \text{(consistent answer)}$$

Because H^+ produced by the K_{a_2} reaction will be negligible, $[H^+] = 1.0 \times 10^{-3}$ and pH = 3.00.

109. Because K_{a_2} for H_2S is so small, we can ignore the H^+ contribution from the K_{a_2} reaction.

$$H_2S \rightleftharpoons H^+ \quad HS^- \qquad K_{a_1} = 1.0 \times 10^{-7}$$

Initial	0.10 *M*	~0	0
Equil.	$0.10 - x$	x	x

$$K_{a_1} = 1.0 \times 10^{-7} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10},\ x = [H^+] = 1.0 \times 10^{-4};\ \text{assumptions good.}$$

$pH = -\log(1.0 \times 10^{-4}) = 4.00$

Use the K_{a_2} reaction to determine $[S^{2-}]$.

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

Initial	$1.0 \times 10^{-4}\ M$	$1.0 \times 10^{-4}\ M$	0
Equil.	$1.0 \times 10^{-4} - x$	$1.0 \times 10^{-4} + x$	x

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

$x = [S^{2-}] = 1.0 \times 10^{-19}$ *M*; 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

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

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 1.2×10^{-2} *M*. The total amount of H^+ present is:

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

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)

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.

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14.7a

106. $H_3C_6H_5O_7 \longleftrightarrow H_2C_6H_5O_7^- + H^+$

$H_2C_6H_5O_7^- \longleftrightarrow HC_6H_5O_7^{2-} + H^+$

$HC_6H_5O_7^{2-} \longleftrightarrow C_6H_5O_7^{3-} + H^+$

108 $H_3AsO_4 \longleftrightarrow H^+ + H_2AsO_4^-$

H_3AsO_4	H^+	$H_2AsO_4^-$
0.20m		
$-x$	$+x$	$+x$
0.20m	$+x$	$+x$

$5.5\times10^{-3} = \frac{x^2}{0.20-x}$

$0.0011 - 0.0055x = x^2$

$0 = x^2 + 0.0055x - 0.0011$

$x = 0.0305m$

$[H_3AsO_4] = 0.20 - 0.0305 = 0.17m$

$[H^+] = 0.0305m$ $[OH^-] = \frac{10^{-14}}{0.0305} = 3.28\times10^{-13}m$

$pH = -\log 0.0305 = 1.52$

$H_2AsO_4^- \longleftrightarrow H^+ + HAsO_4^{2-}$

$H_2AsO_4^-$	H^+	$HAsO_4^{2-}$
0.0305	0.0305	
$-x$	$+x$	$+x$
$0.0305-x$	$0.0305+x$	x

$1.7\times10^{-7} = \frac{(0.0305+x)x}{(0.0305-x)}$

$1.7\times10^{-7}m = x = [HAsO_4^{2-}]$

$0.0305m = [H_2AsO_4^-]$

$HAsO_4^{2-} \longleftrightarrow AsO_4^{2-} + H^+$

$HAsO_4^{2-}$	AsO_4^{2-}	H^+
$1.7\times10^{-7}m$		0.0305m
$-x$	$+x$	$+x$
$1.7\times10^{-7}m - x$	x	$0.0305+x$

$5.1\times10^{-12} = \frac{(0.0305+x)x}{1.7\times10^{-7}-x}$

$[AsO_4^{2-}] = x = 2.84\times10^{-17}m$

14.7b

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$H_2SO_4 \leftrightarrow H^+ + HSO_4^-$ Strong

$5.0\times10^{-3}M \rightarrow +x \quad +x$

$[H^+] = [HSO_4^-] = 5.0\times10^{-3}M$

$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$

HSO_4^-	H^+	SO_4^{2-}
$5.0\times10^{-3}M$	$5.0\times10^{-3}M$	—
$-x$	$+x$	$+x$
$5.0\times10^{-3}M$	$5.0\times10^{-3}+x$	x

$K_{a_2} = 1.2\times10^{-2} = \frac{(5.0\times10^{-3}+x)(x)}{5.0\times10^{-3}-x}$

~~$x = 1.2\times10^{-2}$~~

~~$[H^+] = 5.0\times10^{-3}$~~

CAN'T ASSUME

Quadratic

or $5.0\times10^{-3}x + x^2 - 6.0\times10^{-5} + 1.2\times10^{-2}x$

$0 = x^2 + 1.7\times10^{-2}x - 6.0\times10^{-5}$

$x = 0.0030$

$[H^+] = 5.0\times10^{-3} + 3.0\times10^{-3} = 8.0\times10^{-3}M$

pH = 2.10