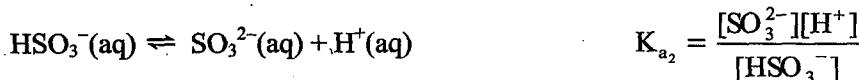
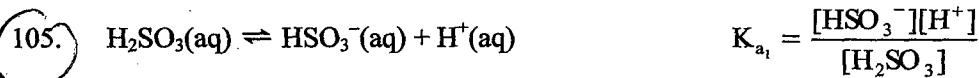
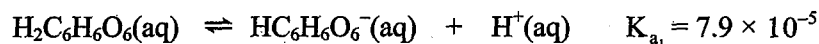


Polyprotic Acids



107. For $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$, $K_{a_1} = 7.9 \times 10^{-5}$ and $K_{a_2} = 1.6 \times 10^{-12}$. Because $K_{a_1} \gg K_{a_2}$, the amount of H^+ produced by the K_{a_2} reaction will be negligible.

$$[\text{H}_2\text{C}_6\text{H}_6\text{O}_6]_0 = \frac{0.500 \text{ g} \times \frac{1 \text{ mol H}_2\text{C}_6\text{H}_6\text{O}_6}{176.12 \text{ g}}}{0.2000 \text{ L}} = 0.0142 \text{ M}$$



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

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

Solving by the method of successive approximations:

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

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

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



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

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

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

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



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

109

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

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

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:

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

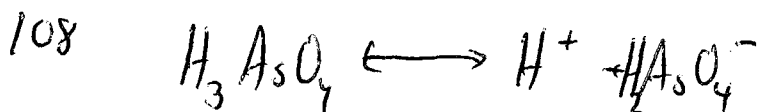
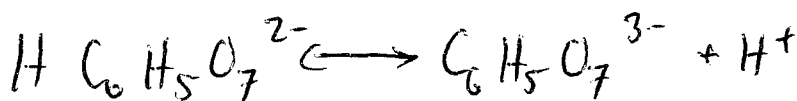
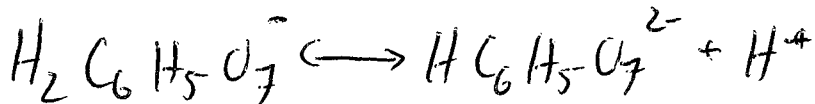
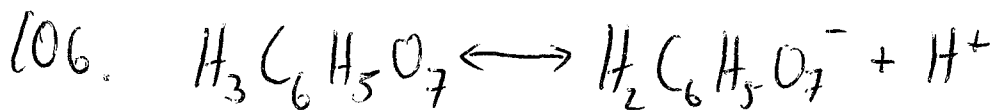
Note: In this problem, H^+ from HSO_4^- could have been ignored. However, this is not usually the case in more dilute solutions of H_2SO_4 .

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.
- Memorize the following strong acids: HCl, HBr, HI, HNO_3 , $HClO_4$, and H_2SO_4
 - Memorize the following strong bases: LiOH, NaOH, KOH, RbOH, CsOH, $Ca(OH)_2$, $Sr(OH)_2$, and Ba(OH)
 - 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.
 - 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.
 - 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



$0.20M$		$+x$		$+x$
$\frac{-x}{0.20M}$		$\frac{+x}{+x}$		$\frac{+x}{+x}$

$$5.5 \times 10^{-3} = \frac{x^2}{0.20 - x}$$

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

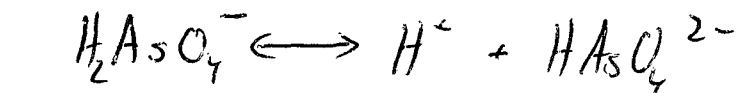
$$0 = x^2 + 0.0055x - 0.0011$$

$$x = 0.0305M$$

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

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

$pH = -\log 0.0305 = 1.52$

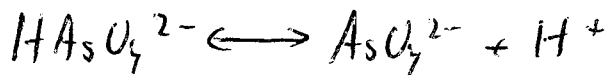


0.0305		0.0305		$+x$
$\frac{-x}{0.0305 - x}$		$\frac{+x}{0.0305 + x}$		$\frac{+x}{x}$

$$1.7 \times 10^{-7} = \frac{(0.0305 - x)x}{(0.0305 + x)}$$

$$1.7 \times 10^{-7}M = x = [HAsO_4^{2-}]$$

$$0.0305M = [H_2AsO_4^-]$$

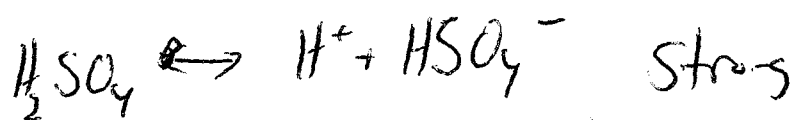


$1.7 \times 10^{-7}M$		$0.0305M$		$+x$
$\frac{-x}{1.7 \times 10^{-7}M - x}$		$\frac{+x}{x}$		$\frac{+x}{0.0305 + x}$

$$5.1 \times 10^{-12} = \frac{(0.0305 - x)x}{1.7 \times 10^{-7} + x}$$

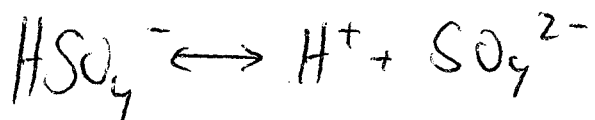
$$[AsO_4^{3-}] = x = 2.84 \times 10^{-17}M$$

112



$$5.0 \times 10^{-3} \text{M} \rightarrow +x \quad +x$$

$$[\text{H}^+] = [\text{HSO}_4^-] = 5.0 \times 10^{-3} \text{M}$$



$5.0 \times 10^{-3} \text{M}$	$5.0 \times 10^{-3} \text{M}$	—
— x	$+x$	$+x$
$5.0 \times 10^{-3} \text{M}$	$5.0 \times 10^{-3} + x$	x

CAN'T ASSUME

Quadratic

$$K_{a2} = 1.2 \times 10^{-2} = \frac{(5.0 \times 10^{-3} + x)(x)}{5.0 \times 10^{-3} - x} \quad \text{or} \quad 5.0 \times 10^{-3} + x^2 - 6.0 \times 10^{-5} + 1.2 \times 10^{-2}$$

~~$x = 1.2 \times 10^{-2}$~~

~~$[\text{H}^+] = 5.0 \times 10^{-3}$~~

$$0 = x^2 + 1.7 \times 10^{-3}x - 6.0 \times 10^{-5}$$

$$x = 0.0030$$

$$[\text{H}^+] = 5.0 \times 10^{-3} + 3.0 \times 10^{-3} = 8.0 \times 10^{-3} \text{M}$$

$$\text{pH} = 2.10$$