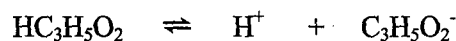


$$[\text{H}^+] = [\text{F}^-] = x = 3.5 \times 10^{-3} \text{ M}; [\text{OH}^-] = K_w/[\text{H}^+] = 2.9 \times 10^{-12} \text{ M}$$

$$[\text{HF}] = 0.020 - x = 0.020 - 0.0035 = 0.017 \text{ M}; \text{pH} = 2.46$$

Note: When the 5% assumption fails, use whichever method you are most comfortable with to solve exactly. The method of successive approximations is probably fastest when the percent error is less than ~25% (unless you have a graphing calculator).

67. $\text{HC}_3\text{H}_5\text{O}_2$ ($K_a = 1.3 \times 10^{-5}$) and H_2O ($K_a = K_w = 1.0 \times 10^{-14}$) are the major species present. $\text{HC}_3\text{H}_5\text{O}_2$ will be the dominant producer of H^+ because $\text{HC}_3\text{H}_5\text{O}_2$ is a stronger acid than H_2O . Solving the weak acid problem:



Initial	0.100 M	~0	0
	x mol/L $\text{HC}_3\text{H}_5\text{O}_2$ dissociates to reach equilibrium		
Change	-x	→ +x	+x
Equil.	0.100 - x	x	x

$$K_a = 1.3 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = [\text{H}^+] = 1.1 \times 10^{-3} \text{ M}; \text{pH} = -\log(1.1 \times 10^{-3}) = 2.96$$

Assumption follows the 5% rule (x is 1.1% of 0.100).

$$[\text{H}^+] = [\text{C}_3\text{H}_5\text{O}_2^-] = 1.1 \times 10^{-3} \text{ M}; [\text{OH}^-] = K_w/[\text{H}^+] = 9.1 \times 10^{-12} \text{ M}$$

$$[\text{HC}_3\text{H}_5\text{O}_2] = 0.100 - 1.1 \times 10^{-3} = 0.099 \text{ M}$$

$$\text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HC}_3\text{H}_5\text{O}_2]_0} \times 100 = \frac{1.1 \times 10^{-3}}{0.100} \times 100 = 1.1\%$$

69. Major species: $\text{HC}_2\text{H}_2\text{ClO}_2$ ($K_a = 1.35 \times 10^{-3}$) and H_2O ; major source of H^+ : $\text{HC}_2\text{H}_2\text{ClO}_2$



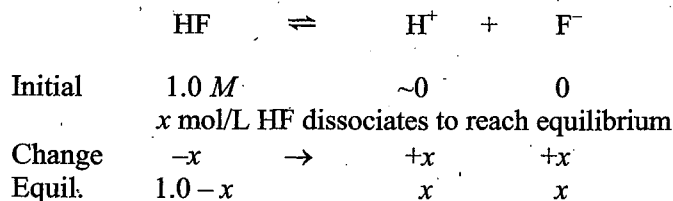
Initial	0.10 M	~0	0
	x mol/L $\text{HC}_2\text{H}_2\text{ClO}_2$ dissociates to reach equilibrium		
Change	-x	→ +x	+x
Equil.	0.10 - x	x	x

$$K_a = 1.35 \times 10^{-3} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}, x = 1.2 \times 10^{-2} \text{ M}$$

Checking the assumptions finds that x is 12% of 0.10, which fails the 5% rule. We must solve $1.35 \times 10^{-3} = x^2/(0.10 - x)$ exactly using either the method of successive approximations or the quadratic equation. Using either method gives $x = [\text{H}^+] = 1.1 \times 10^{-2} \text{ M}$.

$$\text{pH} = -\log[\text{H}^+] = -\log(1.1 \times 10^{-2}) = 1.96.$$

71. HF and HOC_6H_5 are both weak acids with K_a values of 7.2×10^{-4} and 1.6×10^{-10} , respectively. Since the K_a value for HF is much greater than the K_a value for HOC_6H_5 , HF will be the dominant producer of H^+ (we can ignore the amount of H^+ produced from HOC_6H_5 because it will be insignificant).



$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x = [\text{H}^+] = 2.7 \times 10^{-2}\text{ M}; \text{ pH} = -\log(2.7 \times 10^{-2}) = 1.57; \text{ assumptions good.}$$

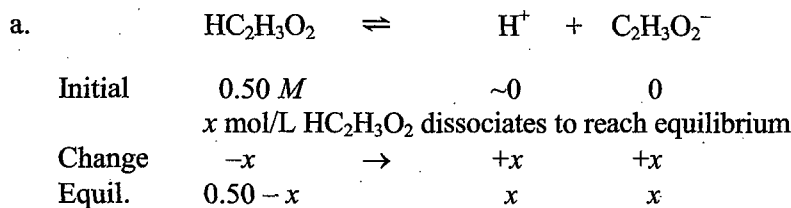
Solving for $[\text{OC}_6\text{H}_5^-]$ using $\text{HOC}_6\text{H}_5 \rightleftharpoons \text{H}^+ + \text{OC}_6\text{H}_5^-$ equilibrium:

$$K_a = 1.6 \times 10^{-10} = \frac{[\text{H}^+][\text{OC}_6\text{H}_5^-]}{[\text{HOC}_6\text{H}_5]} = \frac{(2.7 \times 10^{-2})[\text{OC}_6\text{H}_5^-]}{1.0}, [\text{OC}_6\text{H}_5^-] = 5.9 \times 10^{-9}\text{ M}$$

Note that this answer indicates that only $5.9 \times 10^{-9}\text{ M}$ HOC_6H_5 dissociates, which confirms that HF is truly the only significant producer of H^+ in this solution.

73.

In all parts of this problem, acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) is the best weak acid present. We must solve a weak acid problem.



$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.50 - x} \approx \frac{x^2}{0.50}$$

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 3.0 \times 10^{-3}\text{ M}; \text{ assumptions good.}$$

$$\text{Percent dissociation} = \frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]_0} \times 100 = \frac{3.0 \times 10^{-3}}{0.50} \times 100 = 0.60\%$$

- b. The setup for solutions b and c are similar to solution a except that the final equation is different because the new concentration of $\text{HC}_2\text{H}_3\text{O}_2$ is different.

$$K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 9.5 \times 10^{-4}\text{ M}; \text{ assumptions good.}$$

73

$$\text{Percent dissociation} = \frac{9.5 \times 10^{-4}}{0.050} \times 100 = 1.9\%$$

$$c. K_a = 1.8 \times 10^{-5} = \frac{x^2}{0.0050 - x} \approx \frac{x^2}{0.0050}$$

$$x = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = 3.0 \times 10^{-4} \text{ M}; \text{ check assumptions.}$$

Assumption that x is negligible is borderline (6.0% error). We should solve exactly. Using the method of successive approximations (see Appendix 1 of the text):

$$1.8 \times 10^{-5} = \frac{x^2}{0.0050 - (3.0 \times 10^{-4})} = \frac{x^2}{0.0047}, \quad x = 2.9 \times 10^{-4}$$

$$\text{Next trial also gives } x = 2.9 \times 10^{-4}.$$

$$\text{Percent dissociation} = \frac{2.9 \times 10^{-4}}{5.0 \times 10^{-3}} \times 100 = 5.8\%$$

- d. As we dilute a solution, all concentrations are decreased. Dilution will shift the equilibrium to the side with the greater number of particles. For example, suppose we double the volume of an equilibrium mixture of a weak acid by adding water; then:

$$Q = \frac{\left(\frac{[\text{H}^+]_{\text{eq}}}{2}\right)\left(\frac{[\text{X}^-]_{\text{eq}}}{2}\right)}{\left(\frac{[\text{HX}]_{\text{eq}}}{2}\right)} = \frac{1}{2} K_a$$

$Q < K_a$, so the equilibrium shifts to the right or toward a greater percent dissociation.

- e. $[\text{H}^+]$ depends on the initial concentration of weak acid and on how much weak acid dissociates. For solutions a-c, the initial concentration of acid decreases more rapidly than the percent dissociation increases. Thus $[\text{H}^+]$ decreases.

75

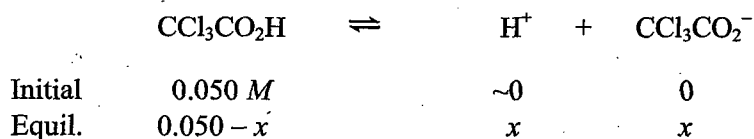
Let HA symbolize the weak acid. Set up the problem like a typical weak acid equilibrium problem.

	HA	⇌	H ⁺	+	A ⁻
Initial	0.15 M		~0		0
	x mol/L HA dissociates to reach equilibrium				
Change	- x	→	+ x		+ x
Equil.	0.15 - x		x		x

If the acid is 3.0% dissociated, then $x = [\text{H}^+]$ is 3.0% of 0.15: $x = 0.030 \times (0.15 \text{ M}) = 4.5 \times 10^{-3} \text{ M}$. Now that we know the value of x , we can solve for K_a .

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.15 - x} = \frac{(4.5 \times 10^{-3})^2}{0.15 - (4.5 \times 10^{-3})} = 1.4 \times 10^{-4}$$

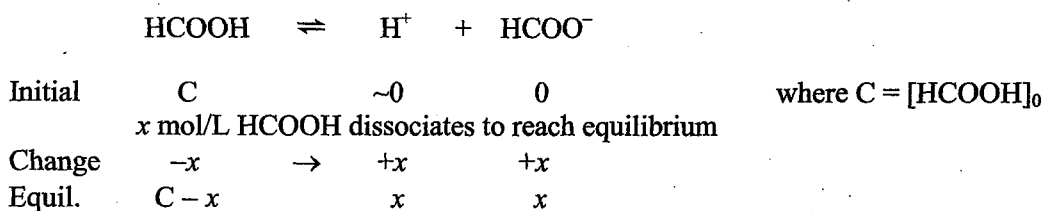
77. HClO_4 is a strong acid with $[\text{H}^+] = 0.040 \text{ M}$. This equals the $[\text{H}^+]$ in the trichloroacetic acid solution. Set up the problem using the K_a equilibrium reaction for $\text{CCl}_3\text{CO}_2\text{H}$.



$$K_a = \frac{[\text{H}^+][\text{CCl}_3\text{CO}_2^-]}{[\text{CCl}_3\text{CO}_2\text{H}]} = \frac{x^2}{0.050 - x}; \text{ from the problem, } x = [\text{H}^+] = 4.0 \times 10^{-2} \text{ M}$$

$$K_a = \frac{(4.0 \times 10^{-2})^2}{0.050 - (4.0 \times 10^{-2})} = 0.16$$

79. Major species: HCOOH and H_2O ; major source of H^+ : HCOOH



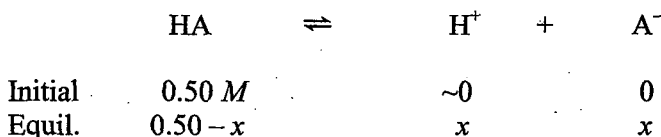
$$K_a = 1.8 \times 10^{-4} = \frac{[\text{H}^+][\text{HCOO}^-]}{[\text{HCOOH}]} = \frac{x^2}{C - x}, \text{ where } x = [\text{H}^+]$$

$$1.8 \times 10^{-4} = \frac{[\text{H}^+]^2}{C - [\text{H}^+]}; \text{ because pH} = 2.70: [\text{H}^+] = 10^{-2.70} = 2.0 \times 10^{-3} \text{ M}$$

$$1.8 \times 10^{-4} = \frac{(2.0 \times 10^{-3})^2}{C - (2.0 \times 10^{-3})}, C - (2.0 \times 10^{-3}) = \frac{4.0 \times 10^{-6}}{1.8 \times 10^{-4}}, C = 2.4 \times 10^{-2} \text{ M}$$

A 0.024 M formic acid solution will have $\text{pH} = 2.70$.

81. $[\text{HA}]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ mol/L}$; solve using the K_a equilibrium reaction.



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.50 - x}; \text{ in this problem, } [\text{HA}] = 0.45 \text{ M so:}$$

$$[\text{HA}] = 0.45 \text{ M} = 0.50 \text{ M} - x, x = 0.05 \text{ M}$$

$$K_a = \frac{(0.05)^2}{0.45} = 6 \times 10^{-3}$$

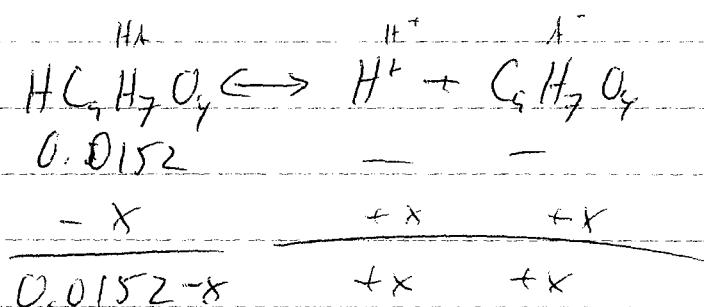
70

14.5a

70 a) 325 mg (ASA) $\text{HC}_9\text{H}_7\text{O}_4$ / tablet \cdot 2 tablets = 650 mg ASA

$$650 \text{ mg} \left(\frac{1 \text{ mol}}{180 \text{ g}} \right) = 3.61 \text{ mmol} \quad K_a = 3.3 \times 10^{-4}$$

$$[\text{ASA}] = \frac{3.61 \text{ mmol}}{237 \text{ mL}} = 0.0152 \text{ M}$$



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad 3.3 \times 10^{-4} = \frac{x^2}{0.0152 - x}$$

$$x = [\text{H}^+] = 0.0022 \text{ M}$$

$$\text{pH} = -\log 0.0022 \text{ M} = 2.65$$