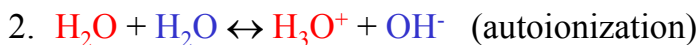
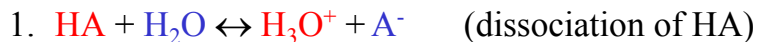


18.4 Solving Problems Involving Weak Acid Equilibria

- In a water solution of the weak acid, HA, there are two sources of H_3O^+ :



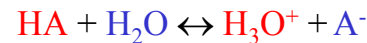
$$\rightarrow [\text{H}_3\text{O}^+]_1 = [\text{A}^-] \quad \text{and} \quad [\text{H}_3\text{O}^+]_2 = [\text{OH}^-]$$

$$\rightarrow [\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_1 + [\text{H}_3\text{O}^+]_2 = [\text{A}^-] + [\text{OH}^-]$$

→ If HA is not very dilute or very weak, the autoionization can be neglected and $[\text{OH}^-] \ll [\text{A}^-]$

$$\Rightarrow [\text{H}_3\text{O}^+] \approx [\text{A}^-] = x$$

- In water solution, the weak acid HA exists in two forms → undissociated (HA) and dissociated (A^-)



→ C_{HA} – total concentration of HA

$$\rightarrow C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$$

$$\Rightarrow [\text{HA}] = C_{\text{HA}} - [\text{A}^-] = C_{\text{HA}} - x$$

→ So $[\text{H}_3\text{O}^+] = x$, $[\text{A}^-] = x$, $[\text{HA}] = C_{\text{HA}} - x$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{C_{\text{HA}} - x}$$

➤ Using equilibrium tables

→ If the autoionization of water is neglected

	[]	$\text{HA} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{A}^-$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
i + c = e	i	C_{HA}	0 0
	c	-x	+x +x
	e	$C_{\text{HA}} - x$	x x

$$K_a = \frac{x^2}{C_{\text{HA}} - x}$$

→ The quadratic equation can be solved for x in order to determine $[\text{H}_3\text{O}^+]$ and pH

→ If x is less than 5% of C_{HA} , x can be neglected in the denominator (5% rule) → works if C_{HA} is relatively large and K_a is small ($C_{\text{HA}}/K_a > 400$)

$$K_a = x^2/C_{\text{HA}} \quad x = (K_a C_{\text{HA}})^{1/2} = [\text{H}_3\text{O}^+]$$

Finding K_a Given Concentrations or pH

Example: If the pH of a 0.20 M HCN solution is 4.95, calculate the K_a of HCN.

$$\rightarrow [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.95} = 1.1 \times 10^{-5} = x$$

$$\rightarrow C_{\text{HCN}} = 0.20 \quad \rightarrow x \ll 5\% \text{ of } C_{\text{HCN}}$$

	[]	$\text{HCN} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CN}^-$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$
i + c = e	i	0.20	0 0
	c	-x	+x +x
	e	0.20 - x	x x

$$K_a = \frac{x^2}{C_{\text{HCN}} - x} \approx \frac{x^2}{C_{\text{HCN}}}$$

$$\Rightarrow K_a = x^2/C_{\text{HCN}} = (1.1 \times 10^{-5})^2/0.20 = \mathbf{6.3 \times 10^{-10}}$$

[Note: $C_{\text{HA}}/K_a = 0.20/6.3 \times 10^{-10} = 3.2 \times 10^8 \gg 400$]

Finding Concentrations and pH Given K_a

Example: What is the pH of a **0.30 M** HF solution? ($K_a = 6.8 \times 10^{-4}$ for HF)

[]	HF + H ₂ O ↔ H ₃ O ⁺ + F ⁻		
<i>i</i>	0.30	0	0
<i>c</i>	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
<i>e</i>	0.30 - <i>x</i>	<i>x</i>	<i>x</i>

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

$$K_a = \frac{x^2}{C_{\text{HF}} - x} \approx \frac{x^2}{C_{\text{HF}}}$$

→ $C_{\text{HF}} = 0.30$ → assume $x < 5\%$ of **0.30**

⇒ $x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 0.30)^{1/2} = 1.4 \times 10^{-2} = [\text{H}_3\text{O}^+]$

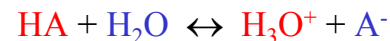
⇒ $pH = -\log[\text{H}_3\text{O}^+] = -\log(1.4 \times 10^{-2}) = \mathbf{1.85}$

[Check assumption: $(1.4 \times 10^{-2} / 0.30) \times 100 = 4.8\% < 5\%$]

[Note: $C_{\text{HF}} / K_a = 0.30 / 6.8 \times 10^{-4} = 441 > 400$]

Extent of Acid Dissociation

• Percent dissociation

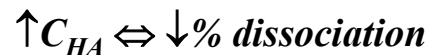


→ $C_{\text{HA}} = [\text{HA}] + [\text{A}^-]$ → $[\text{A}^-] \approx [\text{H}_3\text{O}^+]$

→ $[\text{A}^-] = x$ (dissociated form of the acid)

$$\% \text{ dissociated} = \frac{[\text{A}^-]}{C_{\text{HA}}} \times 100 = \frac{[\text{H}_3\text{O}^+]}{C_{\text{HA}}} \times 100 = \frac{x}{C_{\text{HA}}} \times 100$$

➤ For a given acid, $\%$ dissociated decreases with increasing the total concentration of the acid, C_{HA}



Example: Calculate the $\%$ dissociation for two HF solutions with concentrations **0.30** and **3.0 M**. ($K_a = 6.8 \times 10^{-4}$ for HF)

→ For the **0.30 M** HF from the previous example:

$x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 0.30)^{1/2} = 1.4 \times 10^{-2} = [\text{H}_3\text{O}^+]$

$\% \text{ dissociated} = (1.4 \times 10^{-2} / 0.30) \times 100 = \mathbf{4.8\%}$

→ For the **3.0 M** HF similarly:

$x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 3.0)^{1/2} = 4.5 \times 10^{-2} = [\text{H}_3\text{O}^+]$

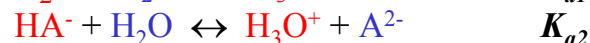
$\% \text{ dissociated} = (4.5 \times 10^{-2} / 3.0) \times 100 = \mathbf{1.5\%}$

⇒ Increasing the concentration from 0.30 to 3.0 M decreases the $\%$ dissociated from 4.8 to 1.5%

The Behavior of Polyprotic Acids

• **Polyprotic Acids** – can donate more than one proton (H_2SO_4 , H_3PO_4 , ...)

– For a general diprotic acid, H_2A



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

➤ Almost all polyprotic acids (except H_2SO_4) are weak in all stages of dissociation and become weaker with each successive dissociation

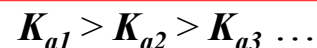


Table 18.5 Successive K_a Values for Some Polyprotic Acids at 25°C

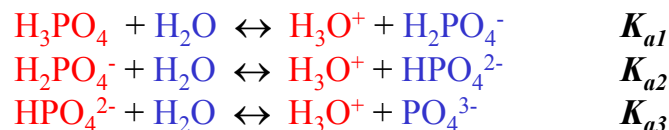
Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($H_2C_2O_4$)		5.6×10^{-2}	5.4×10^{-5}	
Phosphorous acid (H_3PO_3)		3×10^{-2}	1.7×10^{-7}	
Sulfurous acid (H_2SO_3)		1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)		7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)		4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)		9×10^{-8}	1×10^{-17}	

ACID STRENGTH ↑

➤ The second and third dissociations are less pronounced because it's harder to remove an H^+ from negatively charged ions

➤ Equilibrium calculations are greatly simplified by **neglecting subsequent dissociations** since they contribute negligible amounts of H_3O^+

Example: Calculate the pH and the concentrations of all ionized forms for a **0.10 M** H_3PO_4 solution. ($K_{a1} = 7.2 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$, $K_{a3} = 4.2 \times 10^{-13}$)



→ Consider only the first dissociation to get the pH

	H_3PO_4	H_2O	\leftrightarrow	H_3O^+	$+$	$H_2PO_4^-$	
<i>i</i>	0.10			0		0	$K_{a1} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$
<i>c</i>	-x			+x		+x	
<i>e</i>	0.10 - x			x		x	

$$K_{a1} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

→ Assume $x < 5\%$ of 0.10

$$\Rightarrow x = (K_{a1} \times 0.10)^{1/2} = (7.2 \times 10^{-3} \times 0.10)^{1/2} = 2.7 \times 10^{-2}$$

→ Check assumption: $(2.7 \times 10^{-2} / 0.10) \times 100 = 27\% > 5\%$

⇒ The assumption is not justified – must solve the quadratic equation

$$x^2 = K_{a1}(0.10 - x) \quad x^2 + K_{a1}x - 0.10K_{a1} = 0$$

$$x^2 + 7.2 \times 10^{-3}x - 7.2 \times 10^{-4} = 0$$

$$x = \frac{-7.2 \times 10^{-3} + \sqrt{(7.2 \times 10^{-3})^2 + 4 \times 7.2 \times 10^{-4}}}{2} = 2.3 \times 10^{-2}$$

$$\Rightarrow x = [H_3O^+] = [H_2PO_4^-] = 2.3 \times 10^{-2} \text{ M}$$

$$\Rightarrow pH = -\log[H_3O^+] = -\log(2.3 \times 10^{-2}) = 1.63$$

→ To calculate the concentrations of the other species, use the $[H_3O^+]$ and $[H_2PO_4^-]$ from the 1st ionization

$$K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} \quad K_{a3} = \frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$[HPO_4^{2-}] = \frac{K_{a2}[H_2PO_4^-]}{[H_3O^+]} = \frac{6.3 \times 10^{-8} \times 2.3 \times 10^{-2}}{2.3 \times 10^{-2}} = 6.3 \times 10^{-8}$$

$$[PO_4^{3-}] = \frac{K_{a3}[HPO_4^{2-}]}{[H_3O^+]} = \frac{4.2 \times 10^{-13} \times 6.3 \times 10^{-8}}{2.3 \times 10^{-2}} = 1.1 \times 10^{-18}$$