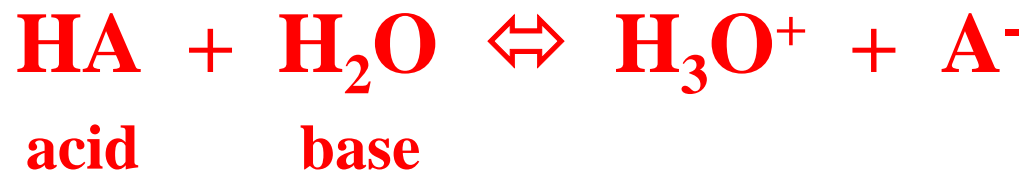


Chapter 16

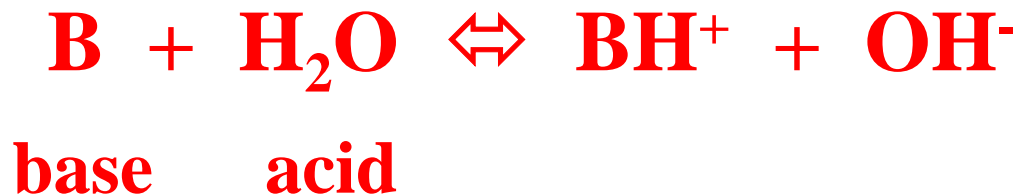
Acids and Bases

Water's Role as Acid or Base

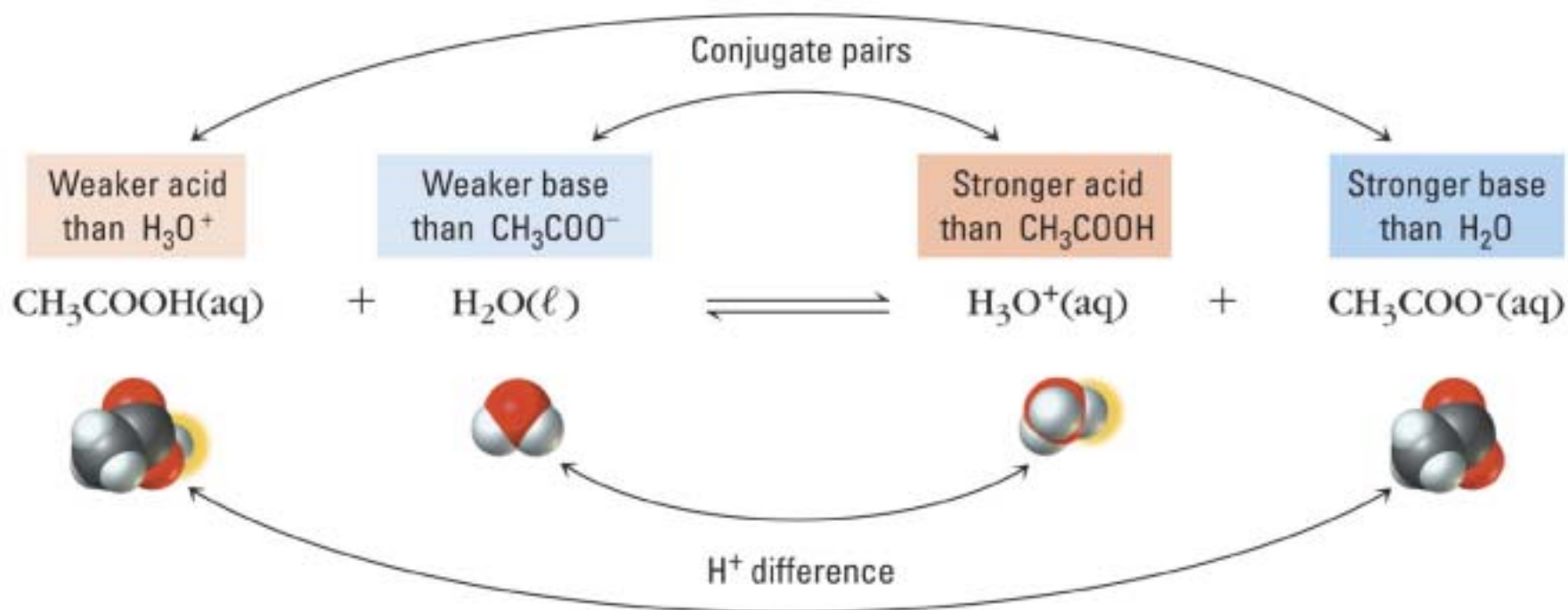
Water acting as a *Base*



Water acting as an *Acid*



Conjugate Acid-Base Pairs



Strong vs. Weak Acids and Bases

strong acid

- completely ionized

weak acid

- partially ionized

Autoionization of Water



$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

$$K_w = K [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Autoionization of Water

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

for a neutral solution

$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+] = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+]^2 = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7}$$

$$-\log([\text{H}_3\text{O}^+]) = -\log(1.0 \times 10^{-7})$$

$$\text{pH} = -\log([\text{H}_3\text{O}^+]) = 7.00$$

Autoionization of Water

a solution is considered acidic when

$$[\text{H}_3\text{O}^+] > 1.0 \times 10^{-7} \text{ M}$$

$$[\text{OH}^-] < 1.0 \times 10^{-7} \text{ M}$$

a solution is considered basic when

$$[\text{H}_3\text{O}^+] < 1.0 \times 10^{-7} \text{ M}$$

$$[\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}$$

Concentration Scales

a solution is considered acidic when

$$\text{pH} < 7 \quad \text{and} \quad \text{pOH} > 7$$

a solution is considered basic when

$$\text{pH} > 7 \quad \text{and} \quad \text{pOH} < 7$$

$$\text{pK}_w = \text{pH} + \text{pOH} = 14.00$$

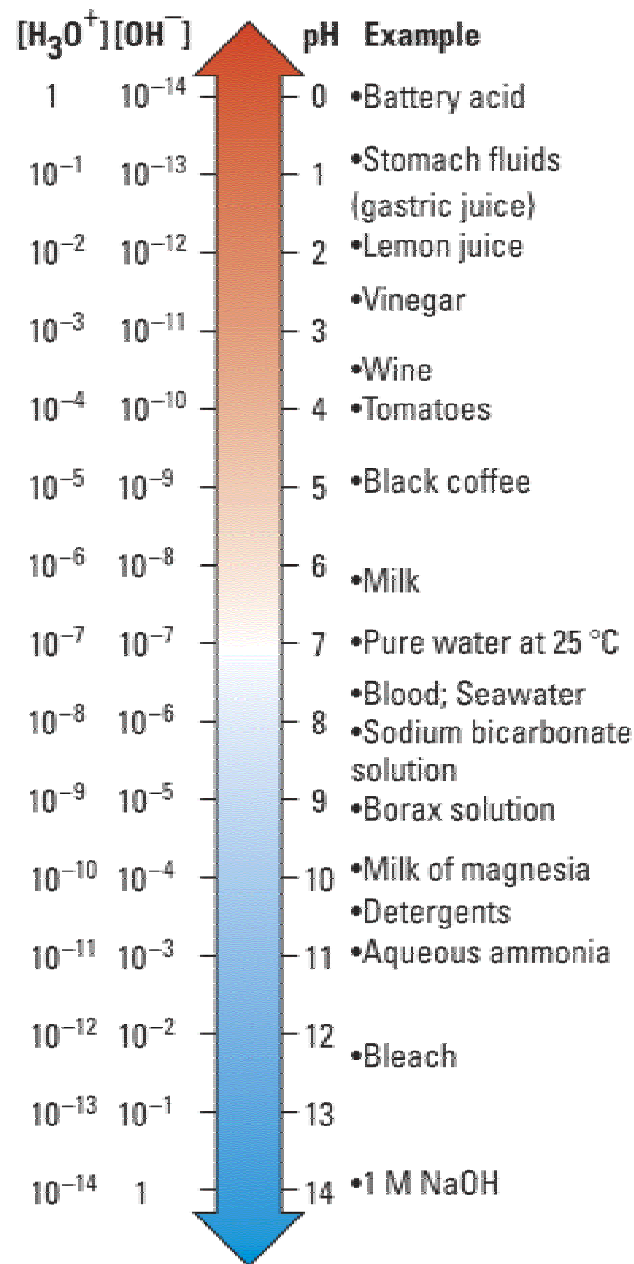
pH Scale (-2 ~ +16)

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

pOH Scale (-2 ~ +16)

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

pH of Aqueous Solutions



EXAMPLE: What is the pH of a solution that has a $[\text{H}_3\text{O}^+] = 0.435 \text{ M}$?

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(0.435) = 0.362$$

EXAMPLE: What is the pH of a solution that has a $[\text{OH}^-] = 25\text{M}$?

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(25) = -1.40$$

$$\begin{aligned}\text{pH} &= 14.00 - \text{pOH} = 14.00 - (-1.40) \\ &= 15.40\end{aligned}$$

Acid Dissociation Constant



$$K = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{H}_2\text{O}][\text{HC}_2\text{H}_3\text{O}_2]}$$

$$K_a = K \times [\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

Base Dissociation Constant



$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{H}_2\text{O}][\text{NH}_3]}$$

$$K_b = K \times [\text{H}_2\text{O}] = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

Relative Strengths of Acid and Bases

Strong 100% ionized (H ⁺ completely donated to water)		Extremely weak (negligible H ⁺ acceptance from water)		
Conjugate acid		Conjugate base		
Strong	H ₂ SO ₄	HSO ₄ ⁻	Extremely weak	
	HBr	Br ⁻		
	HCl	Cl ⁻		
	HNO ₃	NO ₃ ⁻		
Acid strength increasing ↑	H ₃ O ⁺	H ₂ O	Base strength increasing ↓	
	H ₂ SO ₃ (sulfurous)	HSO ₃ ⁻		
	HSO ₄ ⁻	SO ₄ ²⁻		
	H ₃ PO ₄ (phosphoric)	H ₂ PO ₄ ⁻		
	HF (hydrofluoric)	F ⁻		
	HNO ₂ (nitrous)	NO ₂ ⁻		
	CH ₃ COOH (acetic)	CH ₃ COO ⁻		
	H ₂ CO ₃ (carbonic)	HCO ₃ ⁻		
	H ₂ S (hydrosulfuric)	HS ⁻		
	H ₂ PO ₄ ⁻	HPO ₄ ²⁻		
	NH ₄ ⁺	NH ₃		
	HCN	CN ⁻		
	HCO ₃ ⁻	CO ₃ ²⁻		
	H ₂ O	OH ⁻		
	OH ⁻	O ²⁻		
	H ₂	H ⁻		
	CH ₄	CH ₃ ⁻		
Extremely weak		Strong		
Extremely weak (negligible H ⁺ donation to water)		100% reacted with H ⁺ from water		

Ionization Constants for Acids

TABLE 16.2 Ionization Constants for Some Acids and Their Conjugate Bases at 25 °C

Acid name	Acid	$K_a = \frac{[\text{H}_3\text{O}^+][\text{conj base}]}{[\text{conj acid}]}$	Base name	Base	$K_b = \frac{[\text{conj base}][\text{OH}^-]}{[\text{conj base}]}$
Perchloric acid	HClO_4	Large	Perchlorate ion	ClO_4^-	Very small
Sulfuric acid	H_2SO_4	Large	Hydrogen sulfate ion	HSO_4^-	Very small
Hydrochloric acid	HCl	Large	Chloride ion	Cl^-	Very small
Nitric acid	HNO_3	≈ 20	Nitrate ion	NO_3^-	$\approx 5 \times 10^{-16}$
Hydronium ion	H_3O^+	1.0	Water	H_2O	1.0×10^{-14}
Sulfurous acid	H_2SO_3	1.2×10^{-2}	Hydrogen sulfite ion	HSO_3^-	8.3×10^{-13}
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}	Sulfate ion	SO_4^{2-}	8.3×10^{-13}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	Dihydrogen phosphate ion	H_2PO_4^-	1.3×10^{-12}
Hexaquairon(III) ion	$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	6.3×10^{-3}	Pentaquahydroxoiron(III) ion	$\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$	1.6×10^{-12}
Hydrofluoric acid	HF	7.2×10^{-4}	Fluoride ion	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	4.5×10^{-4}	Nitrite ion	NO_2^-	2.2×10^{-11}
Formic acid	HCOOH	1.8×10^{-4}	Formate ion	HCOO^-	5.6×10^{-11}
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	6.3×10^{-5}	Benzoate ion	$\text{C}_6\text{H}_5\text{COO}^-$	1.6×10^{-10}
Acetic acid	CH_3COOH	1.8×10^{-5}	Acetate ion	CH_3COO^-	5.6×10^{-10}
Propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	1.4×10^{-5}	Propanoate ion	$\text{CH}_3\text{CH}_2\text{COO}^-$	7.1×10^{-10}
Hexaaquaaluminum ion	$\text{Al}(\text{H}_2\text{O})_6^{3+}$	7.9×10^{-6}	Pentaquahydroxoaluminum ion	$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$	1.3×10^{-9}
Carbonic acid	H_2CO_3	4.2×10^{-7}	Hydrogen carbonate ion	HCO_3^-	2.4×10^{-8}
Hexaaquacopper(II) ion	$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	1.6×10^{-7}	Pentaquahydroxycopper(II) ion	$\text{Cu}(\text{H}_2\text{O})_5\text{OH}^+$	6.25×10^{-8}
Hydrogen sulfide	H_2S	1×10^{-7}	Hydrogen sulfide ion	HS^-	1×10^{-7}
Dihydrogen phosphate ion	H_2PO_4^-	6.2×10^{-8}	Hydrogen phosphate ion	HPO_4^{2-}	1.6×10^{-7}
Hydrogen sulfite ion	HSO_3^-	6.2×10^{-8}	Sulfite ion	SO_3^{2-}	1.6×10^{-7}
Hypochlorous acid	HClO	3.5×10^{-8}	Hypochlorite ion	ClO^-	2.9×10^{-7}
Hexaqualead(II) ion	$\text{Pb}(\text{H}_2\text{O})_6^{2+}$	1.5×10^{-8}	Pentaquahydroxylead(II) ion	$\text{Pb}(\text{H}_2\text{O})_5\text{OH}^+$	6.7×10^{-7}
Hexaaquacobalt(III) ion	$\text{Co}(\text{H}_2\text{O})_6^{3+}$	1.3×10^{-9}	Pentaquahydroxocobalt(II) ion	$\text{Co}(\text{H}_2\text{O})_5\text{OH}^+$	7.7×10^{-6}
Boric acid	$\text{B}(\text{OH})_3(\text{H}_2\text{O})$	7.3×10^{-10}	Tetrahydroxoborate ion	$\text{B}(\text{OH})_4^-$	1.4×10^{-5}
Ammonium ion	NH_4^+	5.6×10^{-10}	Ammonia	NH_3	1.8×10^{-5}
Hydrocyanic acid	HCN	4.0×10^{-10}	Cyanide ion	CN^-	2.5×10^{-5}
Hexaquairon(II) ion	$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	3.2×10^{-10}	Pentaquahydroxoiron(II) ion	$\text{Fe}(\text{H}_2\text{O})_5\text{OH}^+$	3.1×10^{-5}
Hydrogen carbonate ion	HCO_3^-	4.8×10^{-11}	Carbonate ion	CO_3^{2-}	2.1×10^{-4}
Hexaquanickel(II) ion	$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	2.5×10^{-11}	Pentaquahydroxonickel(II) ion	$\text{Ni}(\text{H}_2\text{O})_5\text{OH}^+$	4.0×10^{-4}
Hydrogen phosphate	HPO_4^{2-}	3.6×10^{-13}	Phosphate ion	PO_4^{3-}	2.8×10^{-2}
Water	H_2O	1.0×10^{-14}	Hydroxide ion	OH^-	1.0
Hydrogen sulfide ion	HS^-	1×10^{-19}	Sulfide ion	S^{2-}	1×10^5
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	Very small	Ethoxide ion	$\text{C}_2\text{H}_5\text{O}^-$	Large
Ammonia	NH_3	Very small	Amide ion	NH_2^-	Large
Hydrogen	H_2	Very small	Hydride ion	H^-	Large
Methane	CH_4	Very small	Methide ion	CH_3^-	Large

Increasing Acid Strength

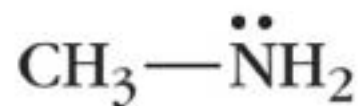
Increasing Base Strength

Influence of Molecular Structure on Acid Strength

Ex. Binary Hydrides

- hydrogen & one other element
- Bond Strengths
 - weaker the bond, the stronger the acid
- Stability of Anion
 - higher the electronegativity, stronger the acid

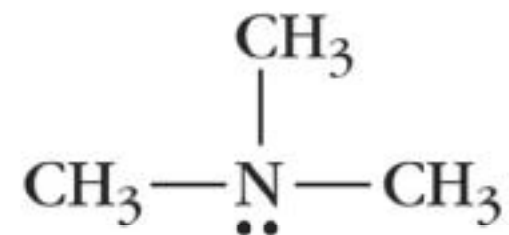
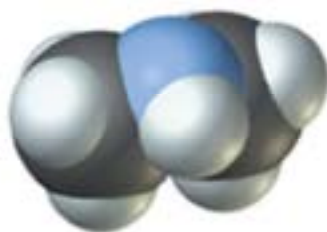
Amines



methylamine



dimethylamine



trimethylamine



Acid-Base Properties of Typical Ions

TABLE 16.5 Acid-Base Properties of Typical Ions in Aqueous Solution

	Neutral		Basic			Acidic
<i>Anions</i>	Cl^- Br^- I^-	NO_3^- ClO_4^-	CH_3COO^- HCOO^- CO_3^{2-} S^{2-} F^-	CN^- PO_4^{3-} HCO_3^- HS^- NO_2^-	SO_4^{2-} HPO_4^{2-} SO_3^{2-} ClO^-	HSO_4^- H_2PO_4^- HSO_3^-
<i>Cations</i>	Li^+ Na^+ K^+	Mg^{2+} Ca^{2+} Ba^{2+}	None			Al^{3+} NH_4^+ Transition metal ions

Polyprotic Acids

- acids where more than one hydrogen per molecule is released

TABLE 16.3 Polyprotic Acids

Acid form	Conjugate base form
H_2S (hydrosulfuric acid)	HS^- (hydrogen sulfide or bisulfide ion)
H_3PO_4 (phosphoric acid)	H_2PO_4^- (dihydrogen phosphate ion)
H_2PO_4^- (dihydrogen phosphate ion)	HPO_4^{2-} (hydrogen phosphate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate or bicarbonate ion)
$\text{H}_2\text{C}_2\text{O}_4$ (oxalic acid)	HC_2O_4^- (hydrogen oxalate ion)
$\text{C}_3\text{H}_5(\text{COOH})_3$ (citric acid)	$\text{C}_3\text{H}_5(\text{COOH})_2\text{COO}^-$ (monocitrate ion)

Acid-Base Chemistry of Some Antacids

TABLE 16.6 The Acid-Base Chemistry of Some Antacids

Compound	Reaction in stomach	Examples of commercial products
Milk of magnesia: $\text{Mg}(\text{OH})_2$ in water	$\text{Mg}(\text{OH})_2(\text{s}) + 2 \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\ell)$	Phillips' Milk of Magnesia
Calcium carbonate: CaCO_3	$\text{CaCO}_3(\text{s}) + 2 \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Ca}^{2+}(\text{aq}) + 3 \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$	Tums, Di-Gel
Sodium bicarbonate: NaHCO_3	$\text{NaHCO}_3(\text{s}) + \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Na}^+(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$	Baking soda, Alka-Seltzer
Aluminum hydroxide: $\text{Al}(\text{OH})_3$	$\text{Al}(\text{OH})_3(\text{s}) + 3 \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Al}^{3+}(\text{aq}) + 6 \text{H}_2\text{O}(\ell)$	Amphojel
Dihydroxyaluminum sodium carbonate: $\text{NaAl}(\text{OH})_2\text{CO}_3$	$\text{NaAl}(\text{OH})_2\text{CO}_3(\text{s}) + 4 \text{H}_3\text{O}^+(\text{aq}) \longrightarrow \text{Na}^+(\text{aq}) + \text{Al}^{3+}(\text{aq}) + 7 \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g})$	Rolaids

EXAMPLE: Calculate the $[\text{H}_3\text{O}^+]$ in an aqueous **0.140 M** acetic acid solution.



$$C_{\text{HA}} = \text{0.140 M}$$

$$K_a = \frac{[\text{H}_3\text{O}^+]_e [\text{C}_2\text{H}_3\text{O}_2^-]_e}{[\text{HC}_2\text{H}_3\text{O}_2]_e} = 1.75 \times 10^{-5} \text{ M}$$

$$\text{let } [\text{H}_3\text{O}^+]_e \approx [\text{C}_2\text{H}_3\text{O}_2^-]_e$$

$$[\text{HC}_2\text{H}_3\text{O}_2]_e = \text{0.140M} - [\text{H}_3\text{O}^+]_e$$

$$C_{\text{HA}} = 0.140 \text{ M} \quad K_a = 1.75 \times 10^{-5} \text{ M}$$

$$\text{let } [\text{H}_3\text{O}^+]_e \approx [\text{C}_2\text{H}_3\text{O}_2^-]_e$$

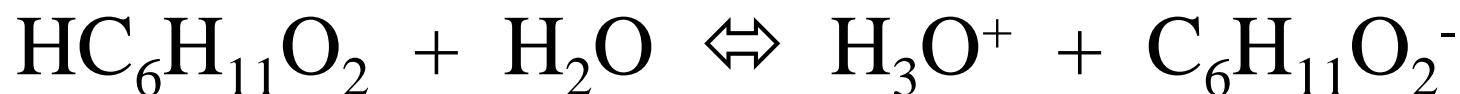
$$[\text{HC}_2\text{H}_3\text{O}_2]_e = 0.140 \text{ M} - [\text{H}_3\text{O}^+]_e$$

using the quadratic equation

$$[\text{H}_3\text{O}^+]_e = \frac{-K_a + (K_a^2 + 4K_a C_{\text{HA}})^{1/2}}{2}$$

$$[\text{H}_3\text{O}^+]_e = 1.56 \times 10^{-3} \text{ M}$$

EXAMPLE: A saturated aqueous solution of caproic acid (mw= 116 g/mol) contains **11 g/L** and has a **pH = 2.94**. What is its K_a ?



$$K_a = \frac{[\text{H}_3\text{O}^+]_e [\text{C}_6\text{H}_{11}\text{O}_2^-]_e}{[\text{HC}_6\text{H}_{11}\text{O}_2]_e} = ?$$

$$[\text{H}_3\text{O}^+]_e = 10^{-\text{pH}} = 10^{-2.94} = 1.1 \times 10^{-3} \text{ M}$$

$$[\text{C}_6\text{H}_{11}\text{O}_2^-]_e = [\text{H}_3\text{O}^+]_e = 1.1 \times 10^{-3} \text{ M}$$

$$\begin{aligned} [\text{HC}_6\text{H}_{11}\text{O}_2]_i &= (11 \text{ g/L})(1 \text{ mol}/116 \text{ g}) \\ &= 9.5 \times 10^{-2} \text{ M} \end{aligned}$$

$$[\text{C}_6\text{H}_{11}\text{O}_2^-]_{\text{e}} = [\text{H}_3\text{O}^+]_{\text{e}} = 1.1 \times 10^{-3} \text{ M}$$

$$[\text{HC}_6\text{H}_{11}\text{O}_2]_{\text{e}} = 9.4 \times 10^{-2} \text{ M}$$

$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^+]_{\text{e}} [\text{C}_6\text{H}_{11}\text{O}_2^-]_{\text{e}}}{[\text{HC}_6\text{H}_{11}\text{O}_2]_{\text{e}}}$$

$$K_{\text{a}} = \frac{(1.1 \times 10^{-3} \text{ M})^2}{9.4 \times 10^{-2} \text{ M}} = 1.3 \times 10^{-5} \text{ M}$$

Solutions of Salts of Weak Acids



$$K_b = \frac{K_w}{K_a} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

