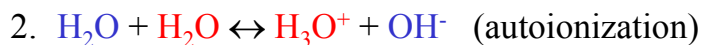
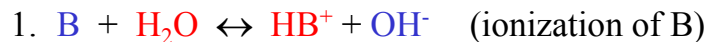


18.5 Solving Problems Involving Weak Base Equilibria

- In a water solution of the weak base, B, there are two sources of OH⁻:



→ $[OH^-]_1 = [HB^+]$ and $[OH^-]_2 = [H_3O^+]$

→ $[OH^-] = [OH^-]_1 + [OH^-]_2 = [HB^+] + [H_3O^+]$

→ If B is not very dilute or very weak, the autoionization can be neglected and $[H_3O^+] \ll [HB^+]$

$$\Rightarrow [OH^-] \approx [HB^+] = x$$

- In water solution, the weak base B exists in two forms → unionized (B) and ionized (HB⁺)



→ C_B – total concentration of B

→ $C_B = [B] + [HB^+]$

$$\Rightarrow [B] = C_B - [HB^+] = C_B - x$$

→ So $[OH^-] = x$, $[HB^+] = x$, $[B] = C_B - x$

$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{x^2}{C_B - x}$$

→ The equation is equivalent to that for weak acids

➤ Using equilibrium tables

→ If the autoionization of water is neglected

	[]	$B + H_2O \leftrightarrow HB^+ + OH^-$		$K_b = \frac{[HB^+][OH^-]}{[B]}$
$i + c = 0$	<i>i</i>	C_B	0	0
	<i>c</i>	-x	+x	+x
	<i>e</i>	$C_B - x$	x	x

$$K_b = \frac{x^2}{C_B - x}$$

→ The quadratic equation can be solved for x in order to determine [OH⁻], pOH and pH

→ If x is less than 5% of C_B , x can be neglected in the denominator (5% rule) → works if C_B is relatively large and K_b is small ($C_B/K_b > 400$)

$$K_b = x^2/C_B \quad x = (K_b C_B)^{1/2} = [OH^-]$$

Finding pH Given K_b

Example: What is the pH of a 0.10 M NH₃ solution? ($K_b = 1.8 \times 10^{-5}$ for NH₃)

	[]	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$		$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$
$i + c = 0$	<i>i</i>	0.10	0	0
	<i>c</i>	-x	+x	+x
	<i>e</i>	0.10 - x	x	x

$$K_b = \frac{x^2}{C_{NH_3} - x} \approx \frac{x^2}{C_{NH_3}}$$

→ $C_{NH_3} = 0.10$ → assume $x < 5\%$ of 0.10

$$\Rightarrow x = (K_b C_{NH_3})^{1/2} = (1.8 \times 10^{-5} \times 0.10)^{1/2} = 1.3 \times 10^{-3} = [OH^-]$$

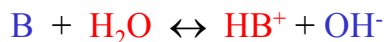
$$\Rightarrow pOH = -\log[OH^-] = -\log(1.3 \times 10^{-3}) = 2.87$$

$$\Rightarrow pH = 14.00 - pOH = 14.00 - 2.87 = \boxed{11.13}$$

[Check assumption: $(1.3 \times 10^{-3}/0.10) \times 100 = 1.3\% < 5\%$]

Extent of Base Ionization

• Percent ionization

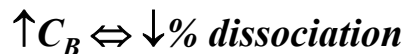


$$\rightarrow C_B = [B] + [HB^+] \quad \rightarrow [HB^+] \approx [OH^-]$$

$$\rightarrow [HB^+] = x \quad (\text{ionized form of the base})$$

$$\% \text{ ionized} = \frac{[HB^+]}{C_B} \times 100 = \frac{[OH^-]}{C_B} \times 100 = \frac{x}{C_B} \times 100$$

➤ For a given base, % *ionized* decreases with increasing the total concentration of the base, C_B



Example: Calculate the % *ionization* for two NH_3 solutions with concentrations **0.10** and **1.0 M**. ($K_b = 1.8 \times 10^{-5}$ for NH_3)

→ For the **0.10 M** NH_3 from the previous example:

$$x = (K_b C_{NH_3})^{1/2} = (1.8 \times 10^{-5} \times 0.10)^{1/2} = 1.3 \times 10^{-3} = [OH^-]$$

$$\% \text{ ionized} = (1.3 \times 10^{-3} / 0.10) \times 100 = \mathbf{1.3\%}$$

→ For the **1.0 M** NH_3 similarly:

$$x = (K_b C_{NH_3})^{1/2} = (1.8 \times 10^{-5} \times 1.0)^{1/2} = 4.2 \times 10^{-3} = [OH^-]$$

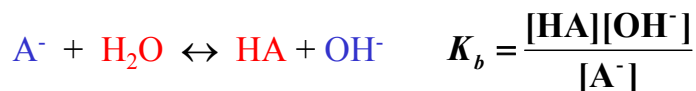
$$\% \text{ ionized} = (4.2 \times 10^{-3} / 1.0) \times 100 = \mathbf{0.42\%}$$

⇒ Increasing the concentration from 0.10 to 1.0 M decreases the % *ionized* from 1.3 to 0.42%

Anions of Weak Acids as Weak Bases

• The anion of the weak acid (HA) is its conjugate base (A^-)

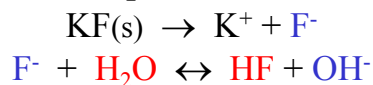
– A^- reacts as a weak base in water:



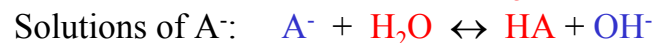
– A^- can be produced in solution by means of the soluble salt, MA, which dissociates completely:



Example: For an aqueous solution of KF



➤ HA and A^- are present in both, solutions of the weak acid HA, and solutions of its anion A^-



➤ Both equilibria are shifted to the left so

➤ Solutions of HA are acidic (H_3O^+) and $[HA] \gg [A^-]$

➤ Solutions of A^- are basic (OH^-) and $[A^-] \gg [HA]$

➤ HA and A^- are a conjugate acid base pair so

$$K_a(\text{HA}) \times K_b(\text{A}^-) = K_w \quad \rightarrow \quad K_b(\text{A}^-) = K_w / K_a(\text{HA})$$

➤ Equilibrium calculations for A^- are carried out using the same method as for the neutral base B

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{C_{A^-} - x}$$

Example: What is the *pH* of a **0.10 M** KF solution? ($K_a = 6.8 \times 10^{-4}$ for HF)



[]	$\text{F}^- + \text{H}_2\text{O} \leftrightarrow \text{HF} + \text{OH}^-$	$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$
<i>i</i>	0.10 0 0	
<i>c</i>	- <i>x</i> + <i>x</i> + <i>x</i>	$K_b = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$
<i>e</i>	0.10 - <i>x</i> <i>x</i> <i>x</i>	

$$\rightarrow K_b(\text{F}^-) = K_w/K_a(\text{HF}) = 1.0 \times 10^{-14}/6.8 \times 10^{-4} = 1.5 \times 10^{-11}$$

$$\Rightarrow x = (K_b \times 0.10)^{1/2} = (1.5 \times 10^{-11} \times 0.10)^{1/2} = 1.2 \times 10^{-6} = [\text{OH}^-]$$

$$\Rightarrow p\text{OH} = -\log[\text{OH}^-] = -\log(1.2 \times 10^{-6}) = 5.92$$

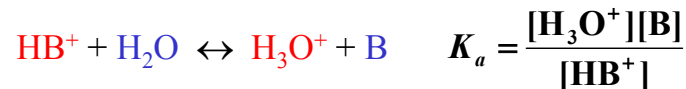
$$\Rightarrow p\text{H} = 14.00 - p\text{OH} = 14.00 - 5.92 = \boxed{8.08} \quad (\text{basic})$$

[Check assumption: $(1.2 \times 10^{-6}/0.10) \times 100 = 0.0012\% < 5\%$]

Cations of Weak Bases as Weak Acids

- The cation of the weak base (B) is its conjugate acid (HB^+)

– HB^+ reacts as a weak acid in water:



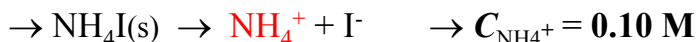
➤ HB^+ and B are a conjugate acid-base pair so

$$K_a(\text{HB}^+) \times K_b(\text{B}) = K_w \rightarrow K_a(\text{HB}^+) = K_w/K_b(\text{B})$$

➤ Equilibrium calculations for HB^+ are carried out using the same method as for the neutral acid HA

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

Example: What is the *pH* of a **0.10 M** NH_4I solution? ($K_b = 1.8 \times 10^{-5}$ for NH_3)



[]	$\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NH}_3$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$
<i>i</i>	0.10 0 0	
<i>c</i>	- <i>x</i> + <i>x</i> + <i>x</i>	$K_a = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$
<i>e</i>	0.10 - <i>x</i> <i>x</i> <i>x</i>	

$$K_a(\text{NH}_4^+) = K_w/K_b(\text{NH}_3) = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

$$\Rightarrow x = (K_a \times 0.10)^{1/2} = (5.6 \times 10^{-10} \times 0.10)^{1/2} = 7.5 \times 10^{-6}$$

$$\Rightarrow [\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$$

$$\Rightarrow p\text{H} = -\log[\text{H}_3\text{O}^+] = -\log(7.5 \times 10^{-6}) = \boxed{5.13} \quad (\text{acidic})$$

[Check assumption: $(7.5 \times 10^{-6}/0.10) \times 100 = 0.0075\% < 5\%$]

18.6 Molecular Properties and Acid Strength

- Binary acids** (H_nX) – consist of H and a second element, X (HF, HCl, H_2O , H_2S , ...)

➤ **Acid strength increases across a period** (the *EN* of X increases → the H–X bond becomes more polar → greater δ^+ charge on the H → greater attraction of the H to the O atom of H_2O)



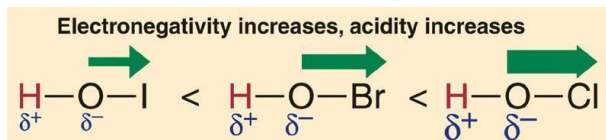
Example: $\text{NH}_3 \ll \text{H}_2\text{O} < \text{HF}$

➤ **Acid strength increases down a group** (X becomes larger → the H–X bond becomes longer and weaker → the H^+ comes off more easily)

Example: $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$

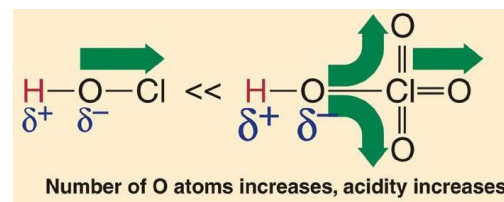
- **Oxoacids** (H_nXO_m) – consist of H, O and a third element, X ($HClO_2$, H_2SO_4 , H_3PO_4 , ...)
 – The acidic H atoms are attached to O atoms
 ➤ For oxoacids with the same # of O atoms, **acid strength increases with increasing the EN of X** (X withdraws electron density from the O–H bond and makes it more polar → greater δ^+ charge on the H → the H^+ comes off more easily)

Example: $HOI < HOBr < HOCl$



- For oxoacids having the same X, **acid strength increases with increasing the # of O atoms** (the high *EN* of O draws electron density from the O–H bond and makes it more polar → greater δ^+ charge on the H → the H^+ comes off more easily)

Example: $HClO < HClO_2 \ll HClO_3 < HClO_4$



- Adding more *EN* atoms to the molecule increases the acidity further (**Ex:** $CH_3COOH < CF_3COOH$)

Acidity of Hydrated Metal Ions

- Metal ions are hydrated in water solutions
 – If the ion is **small and highly charged** (M^{2+} or M^{3+}), it draws electron density from the bound water molecules → H^+ can be released → **acidic**

Example: $AlCl_3(s) + 6H_2O(l) \rightarrow Al(H_2O)_6^{3+} + 3Cl^-$

