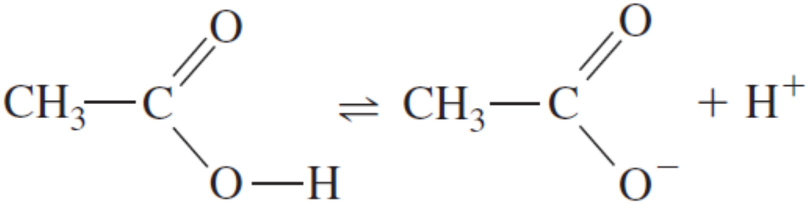
Common Classes of Weak Acids and Bases

- Acetic acid is a typical weak acid


Acetic acid
(HA)

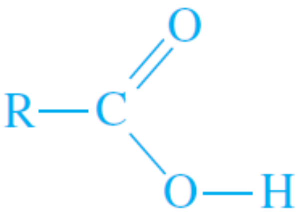
Acetate
(A^-)

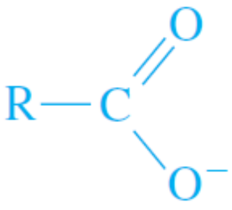
$K_a = 1.75 \times 10^{-5}$

- Acetic acid is a representative carboxylic acid,

→ which has the general formula RCO_2H,

→ where R is an organic substituent.

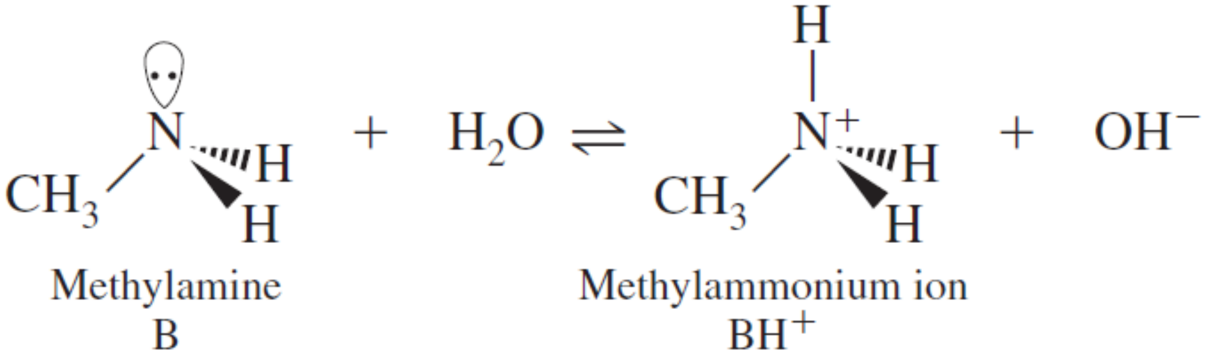

A carboxylic acid
(weak acid, HA)


A carboxylate anion
(weak base, A^-)

- Most carboxylic acids are weak acids,

→ most carboxylate anions are weak bases.

- Methylamine is a typical weak base.

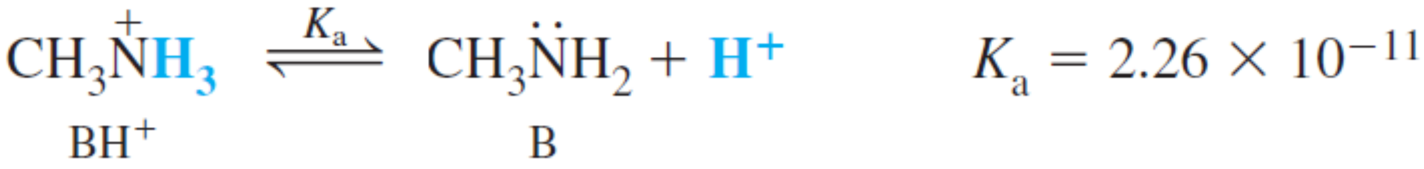


$K_b = 4.47 \times 10^{-4}$

- Amines are nitrogen-containing compounds:

$R\ddot{N}H_2$	a primary amine	RNH_3^+	ammonium ions
$R_2\ddot{N}H$	a secondary amine	$R_2NH_2^+$	
$R_3\ddot{N}$	a tertiary amine	R_3NH^+	

- Amines are weak bases, and ammonium ions are weak acids.



$$\underset{BH^+}{CH_3\overset{+}{N}H_3} \xrightleftharpoons{K_a} \underset{B}{CH_3\ddot{N}H_2} + H^+ \qquad K_a = 2.26 \times 10^{-11}$$

→ The methylammonium ion is the conjugate acid of methylamine

- The salt methylammonium chloride dissociates in aqueous solution to give methylammonium cation and chloride

$$\underset{\substack{\text{Methylammonium}\\ \text{chloride}}}{\mathrm{CH_3\overset{+}{N}H_3Cl^-}(s)} \rightarrow \underset{\substack{\text{Methylammonium}\\ \text{ion}}}{\mathrm{CH_3\overset{+}{N}H_3}(aq)} + \mathrm{Cl^-}(aq)$$

- Methylammonium ion is a weak acid

  → the conjugate acid of methylamine
- Chloride is the conjugate base of HCl, a strong acid.

  → HCl dissociates completely.

  → Cl^- has virtually no tendency to associate with H^+

  → Cl^- has no basic properties
- Methylammonium chloride is acidic

  → because methylammonium ion is an acid and Cl^- is not a base.

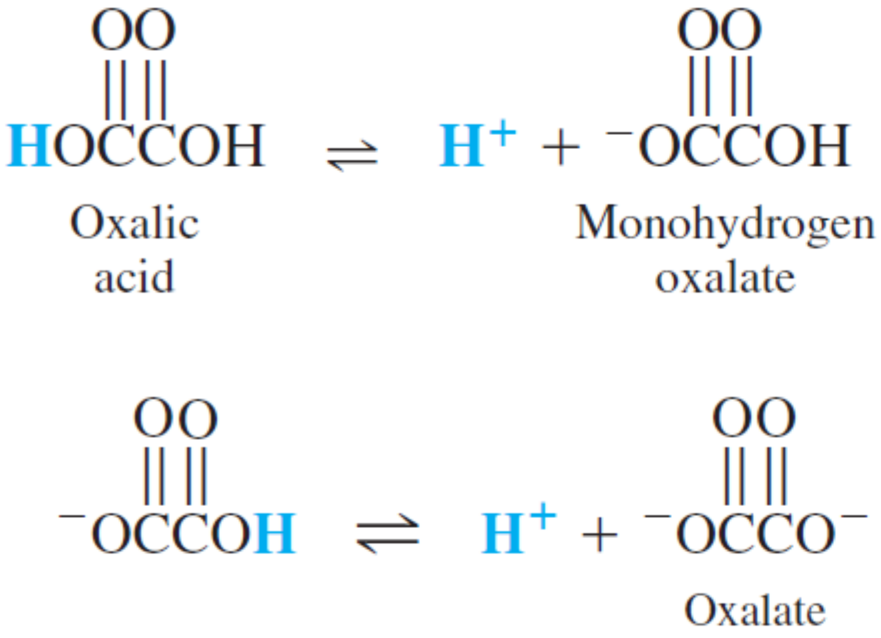
- Metal cations, M^{n+} act as weak acids by acid hydrolysis to form $M(OH)^{(n-1)+}$.

$$M^{n+} + H_2O \underset{}{\overset{K_a}{\rightleftharpoons}} MOH^{(n-1)+} + H^+$$

- Monovalent metal ions are very weak acids (Na^+, $K_a = 10^{-13.9}$).
- Divalent ions tend to be stronger (Fe^{2+}, $K_a = 10^{-9.4}$)

Polyprotic Acids and Bases

- Polyprotic acids and bases are compounds that can donate or accept more than one proton.
- For example, oxalic acid is diprotic and phosphate is tribasic



$$\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \rightleftharpoons \mathrm{H}^+ + {}^-\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \qquad K_{a1} = 5.37 \times 10^{-2}$$

Oxalic acid

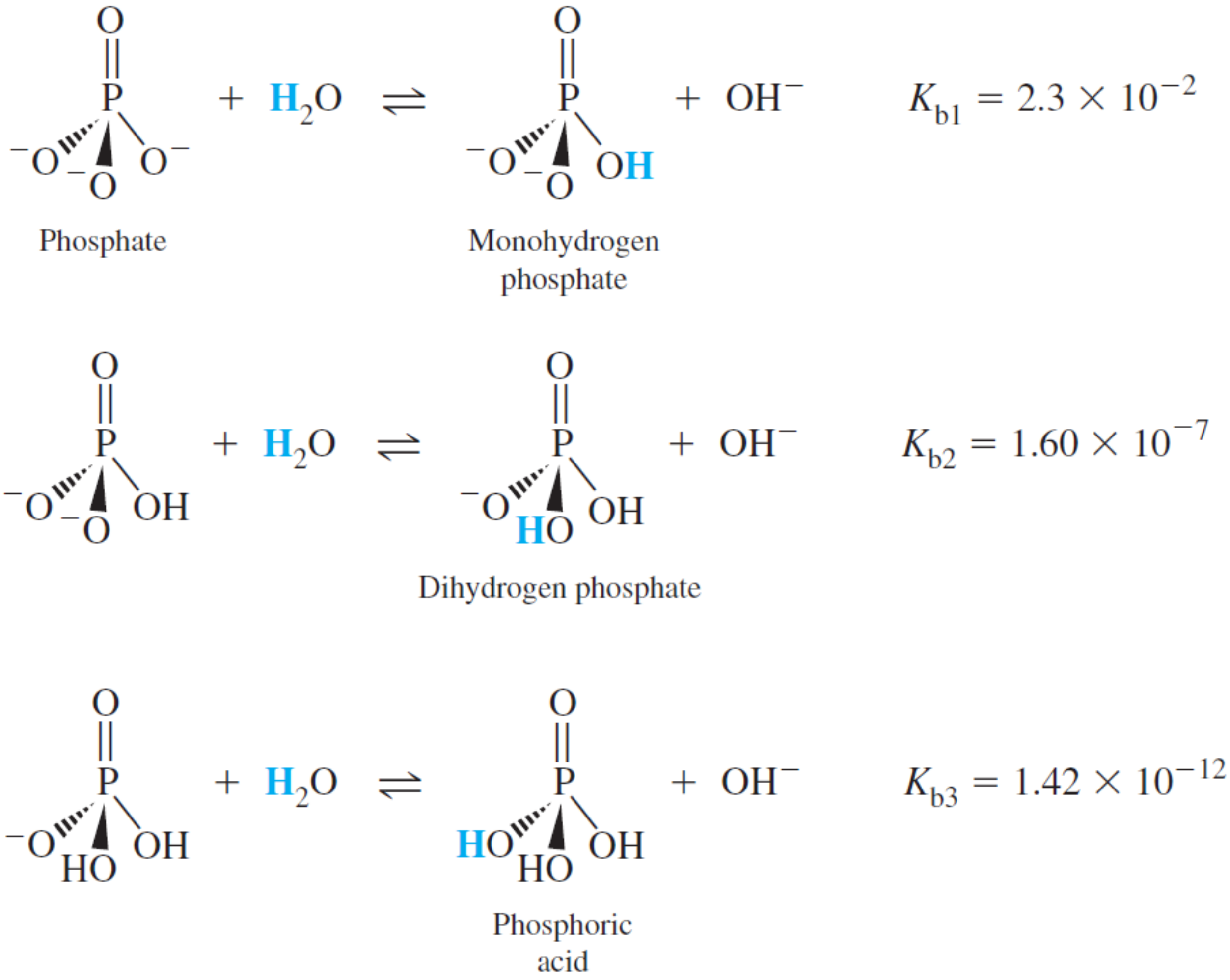
Monohydrogen oxalate

$${}^-\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \rightleftharpoons \mathrm{H}^+ + {}^-\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}^- \qquad K_{a2} = 5.42 \times 10^{-5}$$

Oxalate

Notation for acid and base equilibrium constants:

- K_{a1} refers to the acidic species with the **most** protons
- K_{b1} refers to the basic species with the **least** number of protons.



Relation Between K_a and K_b:

- A most important relation exists between K_a and K_b of a conjugate acid-base pair in aqueous solution.
- We can derive this result with the acid HA and its conjugate base A.

$$\begin{array}{rl}
\cancel{\mathrm{HA}} \rightleftharpoons \mathrm{H^+} + \cancel{\mathrm{A^-}} & K_\mathrm{a} = \dfrac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} \\[2ex]
\underline{\cancel{\mathrm{A^-}} + \mathrm{H_2O} \rightleftharpoons \cancel{\mathrm{HA}} + \mathrm{OH^-}} & K_\mathrm{b} = \dfrac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} \\[2ex]
\mathrm{H_2O} \rightleftharpoons \mathrm{H^+} + \mathrm{OH^-} & K_\mathrm{w} = K_\mathrm{a} \cdot K_\mathrm{b} \\[1ex]
 & \quad = \dfrac{[\mathrm{H^+}][\cancel{\mathrm{A^-}}]}{[\cancel{\mathrm{HA}}]} \cdot \dfrac{[\cancel{\mathrm{HA}}][\mathrm{OH^-}]}{[\cancel{\mathrm{A^-}}]}
\end{array}$$

- When the reactions are added, their equilibrium constants are multiplied to give

Relation between K_a and K_b for a conjugate pair:

$$K_\mathrm{a} \cdot K_\mathrm{b} = K_\mathrm{w}$$

- For a diprotic acid, we can derive relationships between each of two acids and their conjugate bases.

$$\begin{array}{rcll} \cancel{H_2A} & \rightleftharpoons & H^+ + \cancel{HA^-} & K_{a1} \\ \cancel{HA^-} + H_2O & \rightleftharpoons & \cancel{H_2A} + OH^- & K_{b2} \\ \hline H_2O & \rightleftharpoons & H^+ + OH^- & K_w \end{array}$$

$$\begin{array}{rcll} \cancel{HA^-} & \rightleftharpoons & H^+ + \cancel{A^{2-}} & K_{a2} \\ \cancel{A^{2-}} + H_2O & \rightleftharpoons & \cancel{HA^-} + OH^- & K_{b1} \\ \hline H_2O & \rightleftharpoons & H^+ + OH^- & K_w \end{array}$$

The final results are

General relation between K_a and K_b:

$$\boxed{K_{a1} \cdot K_{b2} = K_w}$$

$$\boxed{K_{a2} \cdot K_{b1} = K_w}$$

Analytical Chemistry

Chapter 9. Monoprotic Acid-Base Equilbria

This chapter explains

i) acid-base equilibria

ii) and buffers.

→ we will neglect activity coefficients unless there is a specific point to be made.

9.1 Strong Acids and Bases

- Calculate the pH of 0.10 M KOH.

  → KOH is a strong base (completely dissociated)

  → so $[OH^-] = 0.10$ M

  → Using $K_w = [H^+][OH^-]$,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.10} = 1.0 \times 10^{-13}\,\text{M}$$

$$\text{pH} = -\log[H^+] = 13.00$$

- Finding the pH of other concentrations of KOH is pretty trivial:

$$[H^+] = \frac{K_w}{[OH^-]}$$

$[OH^-]$ (M)	$[H^+]$ (M)	pH
$10^{-3.00}$	$10^{-11.00}$	11.00
$10^{-4.00}$	$10^{-10.00}$	10.00
$10^{-5.00}$	$10^{-9.00}$	9.00

- A generally useful relation is

Relation between pH and pOH:

$$\mathrm{pH} + \mathrm{pOH} = -\log K_w = 14.00 \text{ at } 25^\circ\mathrm{C}$$

The Dilemma

- Calculate the pH of 1.0×10^{-8} M KOH.

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[H^+] = K_w/(1.0 \times 10^{-8}) = 1.0 \times 10^{-6}\,M \Rightarrow pH = 6.00$$

- How can the base KOH produce an acidic solution ($pH < 7$)?

→ there is something wrong with our calculation.

→ In particular, we have not considered the contribution of OH^- from the ionization of water.

→ In pure water, $[OH^-] = 1.0 \times 10^{-7}$ M,

which is greater than the amount of KOH added to the solution.

The Cure

- the systematic treatment of equilibrium.

Step 1 Pertinent reactions.

- The only equilibrium is

$$H_2O \underset{}{\overset{K_w}{\rightleftharpoons}} H^+ + OH^-$$

Step 2 Charge balance.

- The species in solution are K^+, OH^-, and H^+. So,

$$[K^+] + [H^+] = [OH^-]$$

Step 3 Mass balance.

- All K^+ comes from the KOH, so

$$[K^+] = 1.0 \times 10^{-8}\ M$$

Step 4 Equilibrium constant.

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

Step 5 Count.

- There are three equations and three unknowns ($[H^+]$, $[OH^-]$, $[K^+]$),

  → so we have enough information to solve the problem.

Step 6 Solve.

- We seek the pH,

  → so let's set $[H^+] = x$.

  → Writing $[K^+] = 1.0 \times 10^{-8}$ M in the equation below

$$[K^+] + [H^+] = [OH^-]$$

$$\left.\begin{aligned}[OH^-] = [K^+] + [H^+] = 1.0 \times 10^{-8} + x \\ K_w = [H^+][OH^-] = 1.0 \times 10^{-14}\end{aligned}\right\}$$

$$\left.\begin{aligned}[\mathrm{OH}^-] &= [\mathrm{K}^+] + [\mathrm{H}^+] = 1.0 \times 10^{-8} + x \\ K_\mathrm{w} &= [\mathrm{H}^+][\mathrm{OH}^-] = 1.0 \times 10^{-14}\end{aligned}\right\}$$

$$(x)(1.0 \times 10^{-8} + x) = 1.0 \times 10^{-14}$$

$$x^2 + (1.0 \times 10^{-8})x - (1.0 \times 10^{-14}) = 0$$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{(1.0 \times 10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$

$$= 9.6 \times 10^{-8}\,\mathrm{M} \qquad \text{or} \qquad -1.1 \times 10^{-7}\,\mathrm{M}$$

- Rejecting the negative concentration, we conclude that

$$[\mathrm{H}^+] = 9.6 \times 10^{-8}\,\mathrm{M} \Rightarrow \mathrm{pH} = -\log[\mathrm{H}^+] = 7.02$$

- Because 10^{-8} M KOH should be very slightly basic,

  → this pH is reasonable

- Figure 9-1 shows the pH calculated for different concentrations of strong base or strong acid in water.

  → There are three regions:

1. When the concentration is “high” ($\geq 10^{-6}$ M),

   → pH is calculated by just considering the added H^+ or OH^-.

→ That is, the pH of $10^{-5.00}$ M KOH is 9.00.

See Fig 9-1

- There are three regions:

2. When the concentration is "low" (≤ 10^{-8} M),

→ the pH is 7.00.

→ We have not added enough acid or base to change the pH of the water itself.

See Fig 9-1

3. At intermediate concentrations of 10^{-6} to 10^{-8} M,

→ the effects of water ionization and the added acid or base are comparable.

→ Only in this region is a systematic equilibrium calculation necessary.

- The dissociation of water produces 10^{-7} M H^+ and 10^{-7} M OH^-

  → is true only in pure water with no added acid or base.

- In 10^{-4} M HBr,

  → the pH is 4.

- The concentration of OH^- is $[OH^-] = K_w/[H^+] = 10^{-10}$ M.
- But the only source of $[OH^-]$ is dissociation of water.
- If water produces 10^{-10} M OH,

  → it must also produce 10^{-10} M H^+

  → because it makes one H^+ for every OH^-.

- In 10^{-4} M HBr, solution,

  → water dissociation produces only 10^{-10} M OH^- and 10^{-10} M H^+.

  → Any acid or base suppresses water ionization, as predicted by Le Chatelier's principle

9.2 Weak Acids and Bases

- Let's review the meaning of the acid dissociation constant, K_a, for the acid HA:

Weak-acid equilibrium:

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^- \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

- A weak acid is one that is not completely dissociated.

  → That is, the reaction above does not go to completion.

- For a base, B,

  → the base hydrolysis constant, K_b, is defined by the reaction:

Weak-base equilibrium:

$$B + H_2O \overset{K_b}{\rightleftharpoons} BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

Weak-base equilibrium:

$$B + H_2O \underset{}{\overset{K_b}{\rightleftharpoons}} BH^+ + OH^- \qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

- A weak base is one for which the reaction above does not go to completion.

- pK is the negative logarithm of an equilibrium constant:

$$pK_w = -\log K_w$$
$$pK_a = -\log K_a$$
$$pK_b = -\log K_b$$

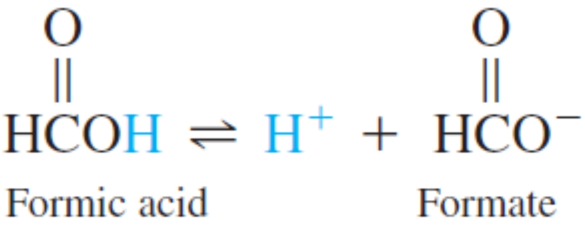
→ As K increases, pK decreases

→ and vice versa.

→ Smaller pK_a means stronger acid

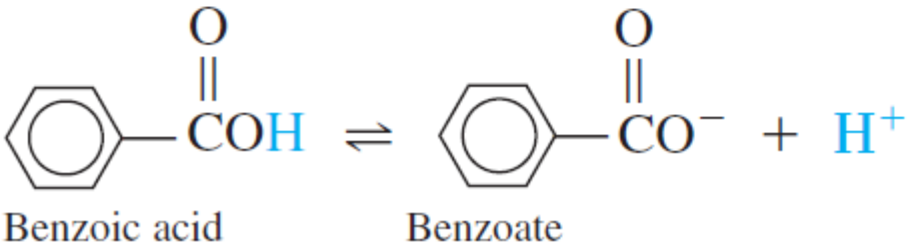
- Comparing formic and benzoic acids,

→ we see that formic acid is stronger, with a larger K_a and smaller pK_a, than benzoic acid.



$$\mathrm{HCOOH} \rightleftharpoons \mathrm{H^+} + \mathrm{HCOO^-}$$

$$K_a = 1.80 \times 10^{-4}$$
$$pK_a = 3.744$$



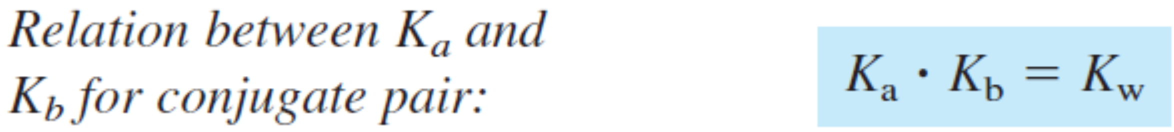
$$K_a = 6.28 \times 10^{-5}$$
$$pK_a = 4.202$$

- The acid HA and its corresponding base, A^-, are said to be a conjugate acid base pair,

  → because they are related by the gain or loss of a proton.

- Similarly, B and BH are a conjugate pair.

- The important relation between K_a and K_b for a conjugate acid-base pair is



Relation between K_a and K_b for conjugate pair:

$$\boxed{K_a \cdot K_b = K_w}$$

Weak is Conjugate to Weak

- The conjugate base of a weak acid is a weak base.
- The conjugate acid of a weak base is a weak acid.

- Consider a weak acid, HA, with $K_a = 10^{-4}$.
- The conjugate base, A^-, has $K_b = K_w/K_a = 10^{-10}$.

  → That is, if HA is a weak acid, A^- is a weak base.

- If K_a were 10^{-5}, then K_b would be 10^{-9}.
- As HA becomes a weaker acid,

  → A^- becomes a stronger base (but never a strong base).

- Conversely, the greater the acid strength of HA,

  → the less the base strength of A^-.

- If either A or HA is weak, so is its conjugate.

- If HA is strong (such as HCl),

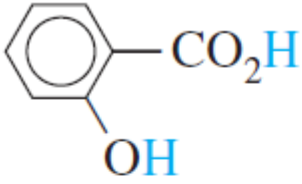
  → its conjugate base (Cl) is so weak that it is not a base at all in water.

- Appendix G gives pK_a for ionic strengths of 0 and 0.1 M.

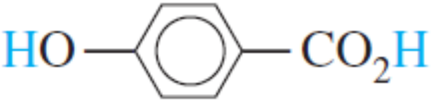
See Appendix G

9.3 Weak-Acid Equilibria

- Let's compare the ionization of ortho- and para-hydroxybenzoic acids:



o-Hydroxybenzoic acid
(salicylic acid)
pK_a = 2.97



p-Hydroxybenzoic acid

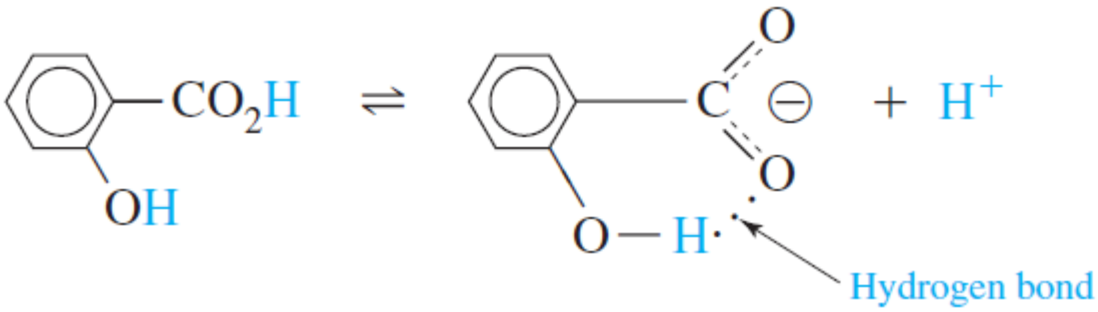
pK_a = 4.54

- Why is the ortho isomer 30 times more acidic than the para isomer?

→ Any effect that increases the stability of the product of a reaction drives the reaction forward.

- In the ortho isomer,

  → the product of the acid dissociation reaction can form a strong, internal hydrogen bond.



- The para isomer cannot form such a bond

  → because the –OH and $–CO_2^-$ groups are too far apart.

- By stabilizing the product,

  → the internal hydrogen bond is thought to make o-hydroxybenzoic acid more acidic than p-hydroxybenzoic acid..

A Typical Weak-Acid Problem

- The problem is to find the pH of a solution of the weak acid HA,
  → given the formal concentration of HA and the value of K_a.
- Let's call the formal concentration F and use the systematic treatment of equilibrium:

Reactions: $\mathrm{HA} \xrightleftharpoons{K_a} \mathrm{H^+} + \mathrm{A^-}$ $\qquad$ $\mathrm{H_2O} \xrightleftharpoons{K_w} \mathrm{H^+} + \mathrm{OH^-}$

Charge balance: $[\mathrm{H^+}] = [\mathrm{A^-}] + [\mathrm{OH^-}]$

Mass balance: $\mathrm{F} = [\mathrm{A^-}] + [\mathrm{HA}]$

Equilibrium expressions: $K_a = \dfrac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$

$K_w = [\mathrm{H^+}][\mathrm{OH^-}]$

→ There are four equations and four unknowns

- For any respectable weak acid,

  → $[H^+]$ from HA will be much greater than $[H^+]$ from H_2O.

- When HA dissociates, it produces A^-.
- When H_2O dissociates, it produces OH^-.

- If dissociation of HA is much greater than dissociation of H_2O,

  → then $[A^-] >> [OH^-]$

$$[H^+] = [A^-] + [\cancel{OH^-}] \quad \Rightarrow \quad [H^+] \approx [A^-]$$

- To solve the problem,

  → first set $[H^+] = x$.

$$[H^+] \approx [A^-]$$

- Charge balance: $[A^-]$ also is equal to x.

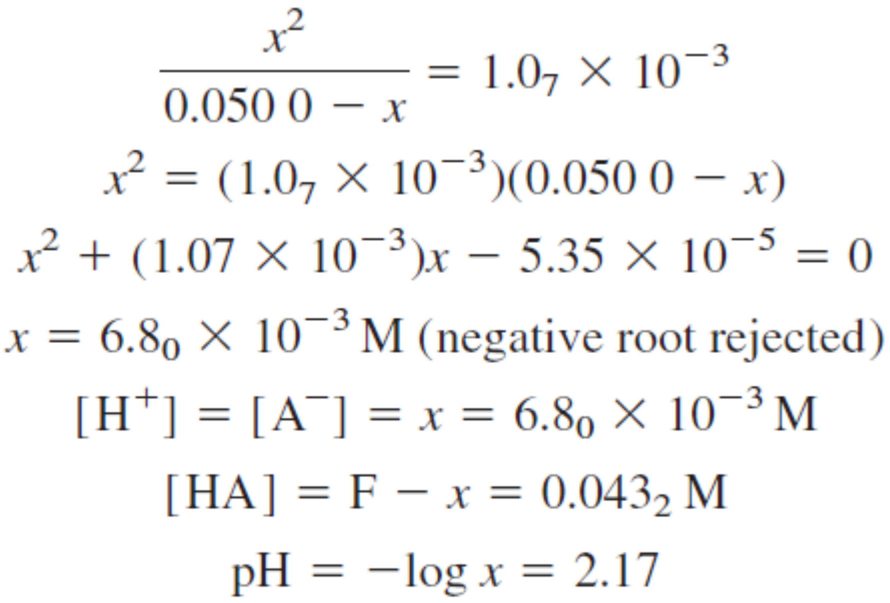
$$F = [A^-] + [HA]$$

- Mass balance: $[HA] = F - [A^-] = F - x$.

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{F - x}$$

- Setting $F = 0.050\,0$ M and $K_a = 1.0_7 \times 10^{-3}$ for o-hydroxybenzoic acid,

  → we can solve the equation



$$\frac{x^2}{0.050\,0 - x} = 1.0_7 \times 10^{-3}$$

$$x^2 = (1.0_7 \times 10^{-3})(0.050\,0 - x)$$

$$x^2 + (1.07 \times 10^{-3})x - 5.35 \times 10^{-5} = 0$$

$$x = 6.8_0 \times 10^{-3}\text{ M (negative root rejected)}$$

$$[\mathrm{H}^+] = [\mathrm{A}^-] = x = 6.8_0 \times 10^{-3}\text{ M}$$

$$[\mathrm{HA}] = \mathrm{F} - x = 0.043_2\text{ M}$$

$$\mathrm{pH} = -\log x = 2.17$$

- Was the approximation justified?

  → The calculated pH is 2.17

  → means that $[\mathrm{OH}^-] = K_w/[\mathrm{H}^+] = 1.5 \times 10^{-12}$ M.

$$[\mathrm{A}^-](\text{from HA dissociation}) = 6.8 \times 10^{-3}\ \mathrm{M}$$

$$\Rightarrow [\mathrm{H}^+]\ \text{from HA dissociation} = 6.8 \times 10^{-3}\ \mathrm{M}$$

$$[\mathrm{OH}^-](\text{from } \mathrm{H_2O} \text{ dissociation}) = 1.5 \times 10^{-12}\ \mathrm{M}$$

$$\Rightarrow [\mathrm{H}^+]\ \text{from } \mathrm{H_2O} \text{ dissociation} = 1.5 \times 10^{-12}\ \mathrm{M}$$

- The assumption that H^+ is derived mainly from HA is excellent.

  → In a solution of a weak acid,

  H^+ is derived almost entirely from HA, not from H_2O.

Fraction of Dissociation

- The fraction of dissociation, α, is defined as the fraction of the acid HA in the form A^-:

Fractions of dissociation of an acid:

$$\alpha = \frac{[A^-]}{[A^-] + [HA]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

- For 0.050 0 M o-hydroxybenzoic acid, we find

$$[A^-](\text{from HA dissociation}) = 6.8 \times 10^{-3}\ \text{M}$$

$$\alpha = \frac{6.8 \times 10^{-3}\ \text{M}}{0.050\,0\ \text{M}} = 0.14$$

→ The acid is 14% dissociated at a formal concentration of 0.050 0 M.