

## Review & chapter 8

Dr. Rjoob

# MONOPROTIC ACID-BASE EQUILIBRIA

## Protic acids and bases

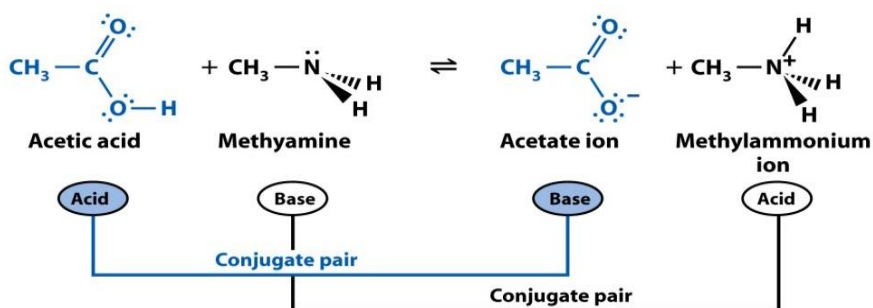
Protic refers to chemistry involving transfer of  $\text{H}^+$  from one molecule to another.

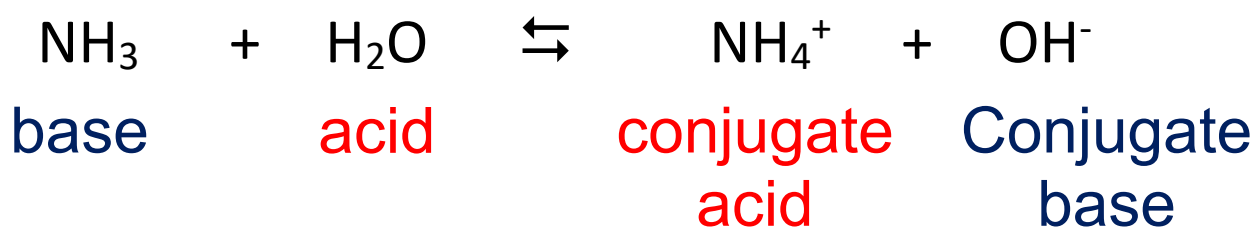
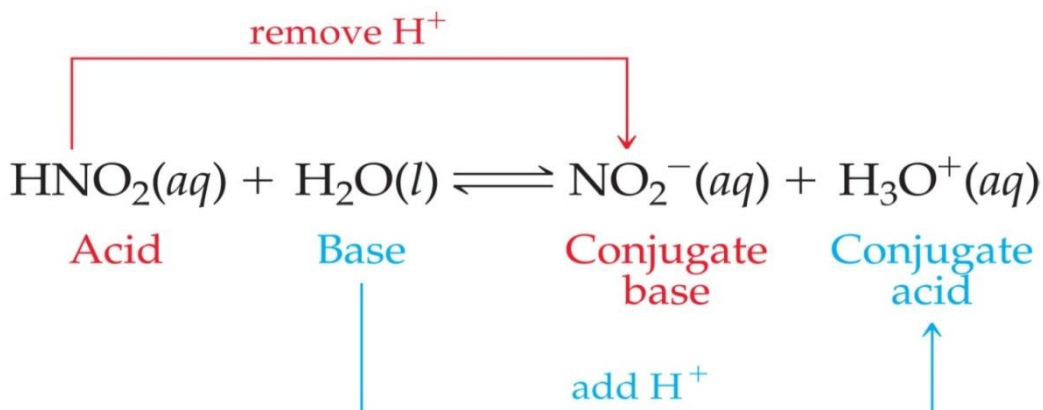
$\text{H}^+$  is called a hydrogen ion (proton) and  $\text{H}_3\text{O}^+$  is called a hydronium ion.

- **Arrhenius**
  - An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions.
  - A base is a substance that, when dissolved in water, increases the concentration of hydroxide ions.
- **Brønsted-Lowry Acids and Bases**
  - An acid is a proton donor.
  - A base is a proton acceptor.
  - A Brønsted-Lowry acid must have a removable (acidic) proton.
  - A Brønsted-Lowry base must have a pair of nonbonding electrons.

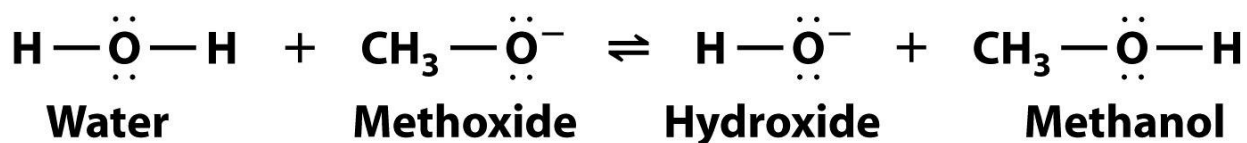
## Conjugate Acids and Bases

- Reactions between acids and bases always yield their conjugate bases and acids.



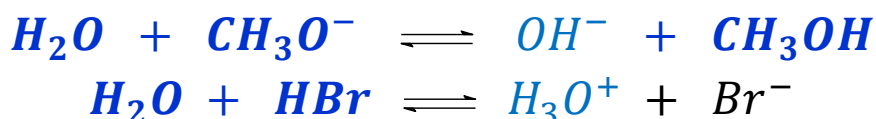


**Q1) Write the conjugate acid-base pairs in the following equations:**



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Q2) What is the conjugate base of each of the following acids:  $\text{HClO}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{PH}_4^+$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{OH}^-$ ,  $\text{H}_2\text{O}$ .

Q3) What is the conjugate acid of each of the following bases:  $\text{CN}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{HCO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{CO}$ ,  $\text{F}^-$ ,  $\text{O}^{2-}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{PO}_4^-$ .

Q4) When  $\text{Li}_2\text{O}$  is dissolved in water, the solution turns basic from the reaction of  $\text{O}^{2-}$  with water:  $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{OH}^-$

Identify the conjugate acid-base pairs.

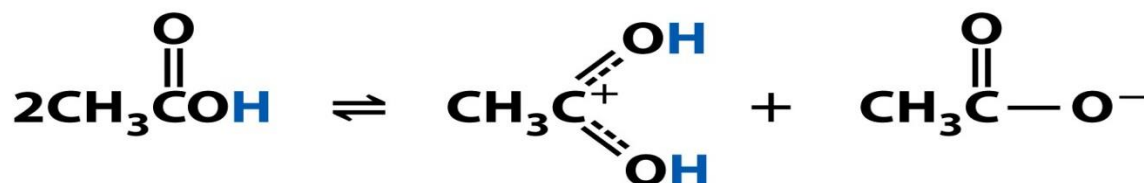
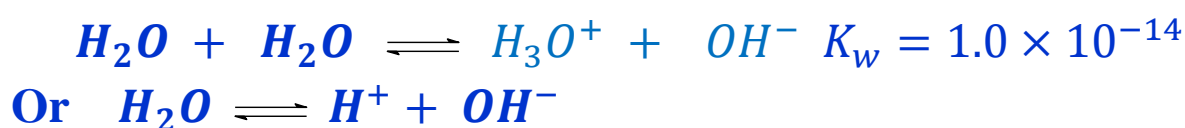
Q5) The conjugate acid of  $\text{NH}_3$  is \_\_\_\_\_

- A)  $\text{NH}_3$       B)  $\text{NH}_2^+$       C)  $\text{NH}_3^+$       D)  $\text{NH}_4^+$

Q6) The conjugate base of  $\text{OH}^-$  is \_\_\_\_\_

- A)  $\text{O}_2$       B)  $\text{O}^-$       C)  $\text{H}_2\text{O}$       D)  $\text{O}^{2-}$

## Autoprotolysis



(in acetic acid)

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## pH

Calculate the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  in pure water at  $25^\circ\text{C}$

$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-] = (x)(x) \rightarrow x = 1.0 \times 10^{-7} \text{ M}$$

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

Q) Find the  $[\text{H}^+]$  in water  $0^\circ\text{C}$  ( $K_w = 1.15 \times 10^{-15}$ ) and at  $100^\circ\text{C}$  ( $K_w = 5.43 \times 10^{-13}$ )

Answer:  $3.4 \times 10^{-8} \text{ M}$  and  $7.4 \times 10^{-7} \text{ M}$

Q) Calculate the concentrations of  $\text{OH}^-$  if  $[\text{H}^+] = 1.0 \times 10^{-3} \text{ M}$

$$K_w = 1.0 \times 10^{-14} = (1.0 \times 10^{-3})[\text{OH}^-] \rightarrow [\text{OH}^-] = 1.0 \times 10^{-11} \text{ M}$$

Q1) Calculate the concentrations of  $H^+(aq)$  in (a) a solution in which  $[OH^-]$  is  $0.00010\text{ M}$  (b) a solution in which  $[OH^-]$  is  $5 \times 10^{-8}\text{ M}$ .

Q2) Calculate the concentrations of  $OH^-(aq)$  in a solution in which (a)  $[H^+] = 2 \times 10^{-6}\text{ M}$ ; (b)  $[H^+] = [OH^-]$ ; (c)  $[H^+] = 100[OH^-]$ ; (d)  $[OH^-] = 10^4[H^+]$

Q3) What is the concentration of hydronium ions( $H_3O^+$ ) in a solution with a hydroxide ion ( $OH^-$ ) concentration of  $2.31 \times 10^{-4}\text{ M}$ ?

A)  $4.33 \times 10^{-11}\text{ M}$  B)  $2.31 \times 10^{10}\text{ M}$  C)  $9.72 \times 10^{-4}\text{ M}$  D)  $1.01 \times 10^{-5}\text{ M}$

pH is defined as the negative base-10 logarithm of the concentration of hydronium ion.

$$\text{pH} = -\log [H_3O^+] \quad \text{OR} \quad \text{pH} = -\log [H^+]$$

In pure water<sup>+</sup>,

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$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

- Since in pure water  $[H_3O^+] = [OH^-]$ ,

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\text{ M}$$

- Therefore, in pure water,

$$\text{pH} = -\log (1.0 \times 10^{-7}) = 7.00$$

- An acid has a higher  $[H_3O^+]$  than pure water, so its pH is  $<7$ .
- A base has a lower  $[H_3O^+]$  than pure water, so its pH is  $>7$ .

Solution Type	$[H^+]\text{ (M)}$	$[OH^-]\text{ (M)}$	pH Value
Acidic	$>1.0 \times 10^{-7}$	$<1.0 \times 10^{-7}$	$<7.00$
Neutral	$=1.0 \times 10^{-7}$	$=1.0 \times 10^{-7}$	$=7.00$
Basic	$<1.0 \times 10^{-7}$	$>1.0 \times 10^{-7}$	$>7.00$

pH increases as  $[H^+]$  decreases

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the  $H^+$  ion concentration of the rainwater?

$$pH = -\log [H^+]$$

$$[H^+] = 10^{-pH} = 10^{-4.82} = 1.5 \times 10^{-5} M$$

What is the pH of an aqueous solution at 25°C in which  $[OH^-]$  is 0.0025 M?

- A) 2.60      B) -2.60      C) 11.40      D) -11.40

What is the pH of an aqueous solution at 25°C in which  $[OH^-]$  is 0.0025 M?

- A) 2.60      B) -2.60      C) 11.40      D) -11.40

$$pOH = -\log [OH^-]$$

$$pK_w = -\log K_w$$

**Because**

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14},$$

**we know that**

$$-\log [H_3O^+] + -\log [OH^-] = -\log K_w = 14.00$$

**or, in other words,**

$$pH + pOH = pK_w = 14.00$$

**In all aqueous solutions (pure water, acidic or basic solutions):**

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ C$$

$$pH + pOH = pK_w = 14.00 \text{ at } 25^\circ C$$

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The  $OH^-$  ion concentration of a blood sample is  $2.5 \times 10^{-7} M$ . What is the pH of the blood?

$$pH + pOH = 14.00$$

$$pOH = -\log [OH^-] = -\log (2.5 \times 10^{-7}) = 6.60$$

$$pH = 14.00 - pOH = 14.00 - 6.60 = 7.40$$

### 7-3 pH Revisited

The definition  $\text{pH} \approx -\log[\text{H}^+]$  in Chapter 6 is not exact. A better definition is

$$\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log[\text{H}^+]\gamma_{\text{H}^+} \quad (7-8)$$

When we measure pH with a pH meter, we are measuring the negative logarithm of the hydrogen ion activity, not its concentration.

### EXAMPLE pH of Pure Water at 25°C

Let's calculate the pH of pure water by using activity coefficients.

**Solution** The relevant equilibrium is



$$K_w = \mathcal{A}_{\text{H}^+} \mathcal{A}_{\text{OH}^-} = [\text{H}^+]\gamma_{\text{H}^+} [\text{OH}^-]\gamma_{\text{OH}^-} \quad (7-10)$$

$\text{H}^+$  and  $\text{OH}^-$  are produced in a 1:1 mole ratio, so their concentrations must be equal. Calling each concentration  $x$ , we write

$$K_w = 1.0 \times 10^{-14} = (x)\gamma_{\text{H}^+}(x)\gamma_{\text{OH}^-}$$

But the ionic strength of pure water is so small that it is reasonable to guess that  $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} = 1$ . Using these values in the preceding equation gives

$$1.0 \times 10^{-14} = (x)(1)(x)(1) = x^2 \Rightarrow x = 1.0 \times 10^{-7} \text{ M}$$

The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are both  $1.0 \times 10^{-7} \text{ M}$ . The ionic strength is  $1.0 \times 10^{-7} \text{ M}$ , so each activity coefficient is very close to 1.00. The pH is

$$\text{pH} = -\log[\text{H}^+]\gamma_{\text{H}^+} = -\log(1.0 \times 10^{-7})(1.00) = 7.00$$

Example: Calculate the pH of water containing 0.10 M KCl Dr. Rjoob

**Solution** Reaction 7-9 tells us that  $[\text{H}^+] = [\text{OH}^-]$ . However, the ionic strength of 0.10 M KCl is 0.10 M. The activity coefficients of  $\text{H}^+$  and  $\text{OH}^-$  in Table 7-1 are 0.83 and 0.76, respectively, when  $\mu = 0.10 \text{ M}$ . Putting these values into Equation 7-10 gives

$$\begin{aligned} K_w &= [\text{H}^+]\gamma_{\text{H}^+} [\text{OH}^-]\gamma_{\text{OH}^-} \\ 1.0 \times 10^{-14} &= (x)(0.83)(x)(0.76) \\ x &= 1.26 \times 10^{-7} \text{ M} \end{aligned}$$

The concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are equal and are both greater than  $1.0 \times 10^{-7} \text{ M}$ . The activities of  $\text{H}^+$  and  $\text{OH}^-$  are not equal in this solution:

$$\begin{aligned} \mathcal{A}_{\text{H}^+} &= [\text{H}^+]\gamma_{\text{H}^+} = (1.26 \times 10^{-7})(0.83) = 1.05 \times 10^{-7} \\ \mathcal{A}_{\text{OH}^-} &= [\text{OH}^-]\gamma_{\text{OH}^-} = (1.26 \times 10^{-7})(0.76) = 0.96 \times 10^{-7} \end{aligned}$$

Finally, we calculate  $\text{pH} = -\log \mathcal{A}_{\text{H}^+} = -\log(1.05 \times 10^{-7}) = 6.98$ .

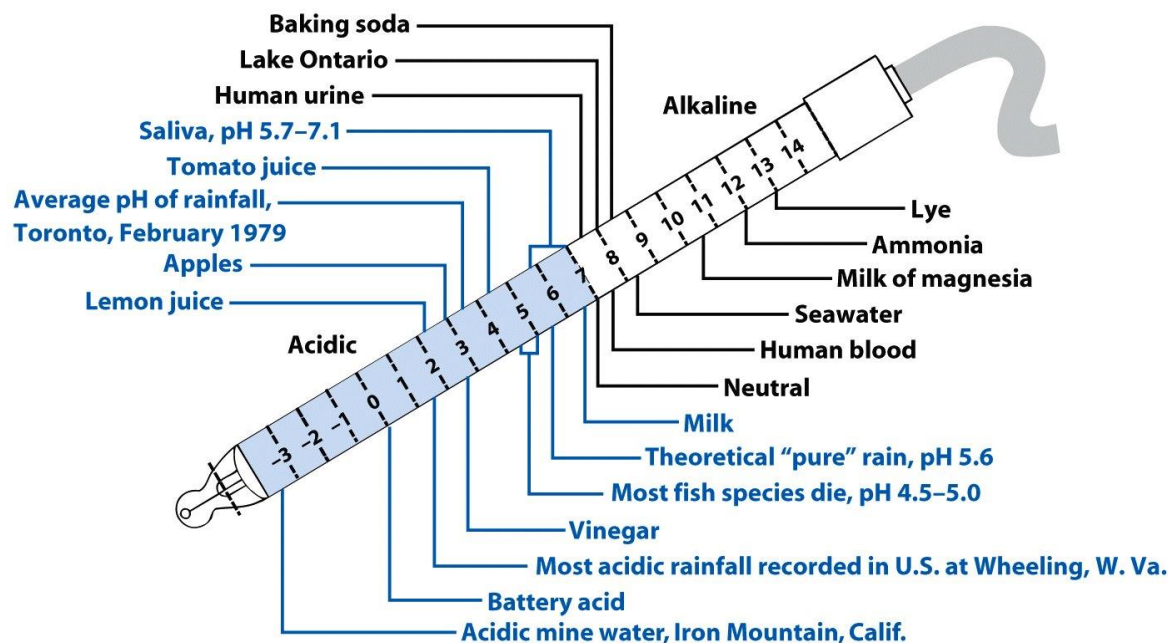
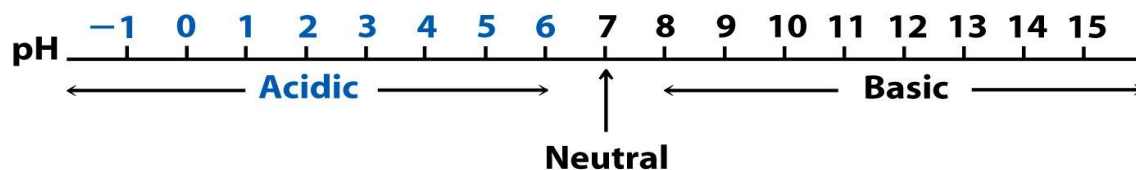


Figure 6-7  
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## 8.1 Strong Acids and Bases

### Strong Acids:

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HCl, HBr, HI, HClO<sub>4</sub>, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> (1st H<sup>+</sup> only)

Completely ionized in dilute solutions:  $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$

**Likewise, strong bases** such as LiOH, NaOH, KOH, RbOH, CsOH, alkoxides (e.g. CH<sub>3</sub>O<sup>-</sup>), and quaternary ammonium hydroxides (e.g. (CH<sub>3</sub>)<sub>4</sub>N-OH) are also completely ionized in dilute aqueous solution.

**Strong Acids:** [H<sub>3</sub>O<sup>+</sup>] equals concentration of strong acid

$\text{pH} = -\log [\text{H}^+]$  (in reality,  $\text{pH} = -\log A_{(\text{H}^+)}$ )

**What is the pH of a 0.10 M solution of HCl?**

$$[H^+] = [HCl] = 0.10 \text{ M}$$

$$\text{pH} = -\log[H^+] = -\log 0.10 = 1.00$$

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**Calculate the pH of a 0.10 M solution of HCl, using activity coefficients.**

$$\mu = 0.10 \text{ M and } \lambda_{H^+} = 0.83 \text{ (from table 7-1)}$$

$$\text{pH} = -\log[H^+] \lambda_{H^+} = -\log (0.10)(0.83) = 1.08$$

Q) Calculate the pH of 0.010 M HBr in 0.090 M KBr. (Answer: 2.08)

What is the concentration of  $OH^-$  ions in a HCl solution whose hydrogen ion concentration is  $1.3 \text{ M}$ ?

$$\text{Answer: } 7.7 \times 10^{-15} \text{ M}$$

**Strong Bases:**  $[OH^-]$  equals concentration of strong base

$$\text{pH} = -\log [H^+], \text{ where } [H^+] \text{ is found from: } [H^+] = \frac{K_w}{[OH^-]}$$

$$\text{or: } \text{pH} = 14 - \text{pOH}$$

**What is the pH of a 0.10 M solution of KOH?**

$$[OH^-] = [KOH] = 0.10 \text{ M}$$

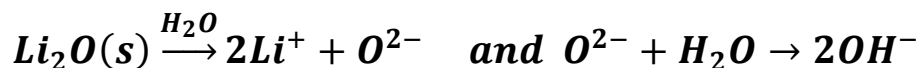
$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

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

$$\text{pH} = -\log[H^+] = -\log(1.0 \times 10^{-13}) = 13.00$$



Calculate the pH of a 0.10 M aqueous solution of  $\text{Li}_2\text{O}$ .



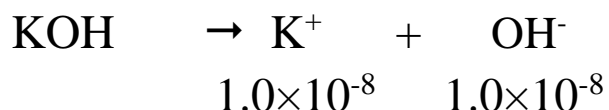
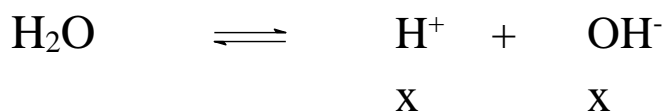
Answer: 13.3

**CAUTION: What is the pH of  $1.0 \times 10^{-8} \text{ M KOH}$ ?**

$$\text{pOH} = -\log 1.0 \times 10^{-8} = 8$$

$\text{pH} = 14 - 8 = 6$  ?? How can the strong base KOH solution produces an acidic solution??

**The contribution of  $\text{OH}^-$  from the dissociation of water has to be taken into account!**



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

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

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

$$x = 9.6 \times 10^{-8} \text{ M}$$

$$\text{pH} = 7.02$$

**Concentration of strong acid or base:**

High ( $> 10^{-6} \text{ M}$ ): use regular formulas

Low ( $< 10^{-8} \text{ M}$ ):  $\text{pH} = 7.00$

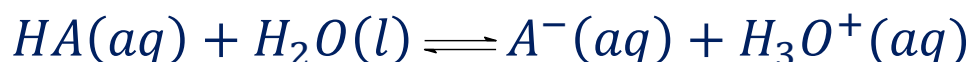
Intermediate ( $10^{-6} > [\text{H}^+] > 10^{-8}$ ): the effects of water ionization and the added acid or base are comparable.

**What is the pH of  $1.0 \times 10^{-8} \text{ M HBr}$ ?**

## 8.2 Weak Acids and Bases

Weak acids are weak proton donors, only partly dissociated in aqueous solution, yielding an equilibrium mixture of weak acid, conjugate base and  $H^+$ ; i.e. the following equilibrium reaction does not go to completion:

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the equilibrium expression would be

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

- This equilibrium constant is called the acid-dissociation constant,  $K_a$ .

The greater the value of  $K_a$  the stronger is the acid.

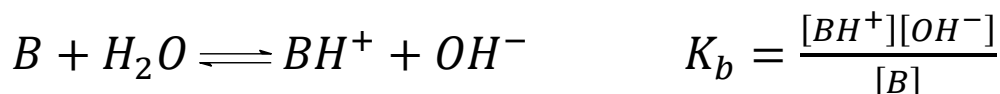
$$pK_a = -\log(K_a)$$

As  $K_a$  increase  $\rightarrow$   $pK_a$  decrease  
- Smaller  $pK_a \rightarrow$  stronger acid

Typical weak acids are carboxylic acids, conjugate acids of weak bases (e.g.  $NH_4^+ \rightleftharpoons NH_3 + H^+$ ) which also include protonated anions from polyprotic acids (e.g.  $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$ )

Often,  $pK_a$  is used instead of  $K_a$ ; a typical  $pK_a$  value for carboxylic acids is  $\sim 4.5$  – the higher the  $pK_a$ , the smaller  $K_a$  and the weaker the acid.

Likewise, for weak bases the following equilibrium does not go to completion and a mixture of weak base, conjugate acid and  $OH^-$  is obtained:



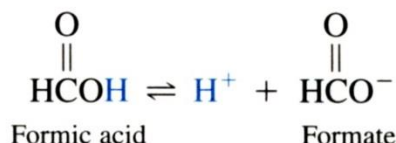
Where  $K_b$  is the base-dissociation constant (the base hydrolysis constant). Again, B and  $BH^+$  are a conjugate acid-base pair

Typical weak bases are amines ( $R - NH_2 + H_2O \rightleftharpoons R - NH_3^+ + OH^-$ ) and conjugate bases (anions) of weak acids (e.g.  $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ )

$$pK_b = -\log(K_b) \quad \text{As } K_b \text{ increase} \rightarrow pK_b \text{ decrease}$$

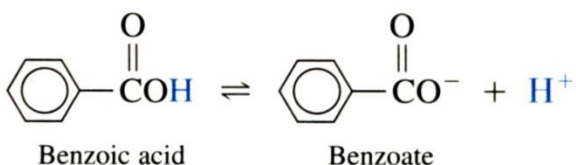
**-Smaller  $pK_b \rightarrow$  stronger base**

➤ Conjugate acid-base pair – related by the gain or loss of a proton



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

$$pK_a = 3.744$$



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

$$pK_a = 4.202$$

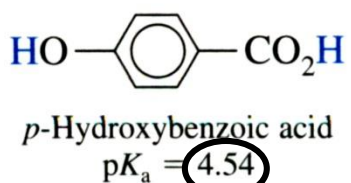
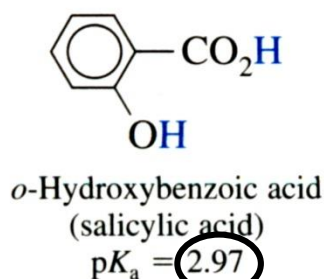
- Conjugate base of a weak acid is a weak base
- Conjugate acid of a weak base is a weak acid
- Conjugate base of a strong acid is a very weak base or salt

### Weak Acid Equilibria

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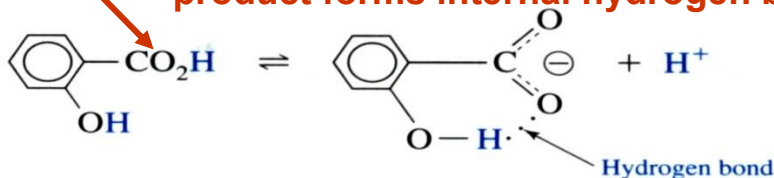
Any Effect that Increases the Stability of the Product Drives the Reaction Forward

➤ Formation of internal hydrogen bond for an acid/base



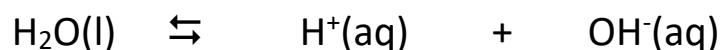
Can't form internal hydrogen bond

**Ortho isomer is stronger acid because product forms internal hydrogen bond**



Relationship between  $K_a$  and  $K_b$ 

$$K_a \times K_b = K_w$$



$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]}$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_a \times K_b = \frac{[NH_3][H^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

For any conjugate acid-base pair:

$$K_a \times K_b = K_w$$

Note: most handbooks list  $pK_a$  values for acids and bases, i.e. for bases the  $pK_a$  of the conjugated acid is listed (see Appendix G in Harris 8th Ed.)

e.g.:  $pK_a$  of  $NH_4^+$  is listed as 9.25; the  $pK_b$  of  $NH_3$  is found as  $14.00 - 9.25 = 4.75$

$pK_a$  of  $CH_3COOH$  is 4.76; the  $pK_b$  of  $CH_3COO^-$  is  $14.00 - 4.76 = 9.24$

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

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

Example)	HA ( $K_a$ )	$A^-$ ( $K_b$ )
	$10^{-4}$	$10^{-10}$
	$10^{-5}$	$10^{-9}$
	$10^{-7}$	$10^{-7}$

As HA becomes a weaker acid,  $A^-$  becomes a stronger base.

(but never a strong base. Recall that  $K_a \times K_b = K_w$ )

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The stronger the acid (base), the weaker its conjugate base (acid)

Strong acids (e.g. HCl) have such weak conjugate bases that they are not considered bases at all ( $Cl^-$  is not a base)

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Q)  $K_a$  for acetic acid is  $1.75 \times 10^{-5}$ . Find  $K_b$  for acetate ion.

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

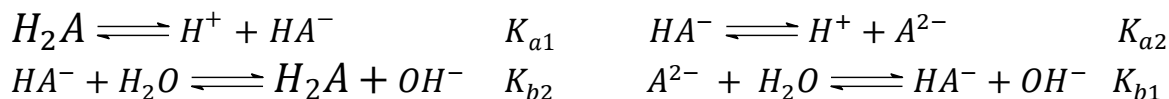
Calculate (a) the base-dissociation constant,  $K_b$ , for the fluoride ion ( $F^-$ ); the acid-dissociation constant,  $K_a$ , for the ammonium ion ( $NH_4^+$ ).  $K_a(HF) = 6.8 \times 10^{-4}$  and  $K_b(NH_3) = 1.8 \times 10^{-5}$ .

Answers:  $K_b(F^-) = 1.5 \times 10^{-11}$  and  $K_a(NH_4^+) = 5.6 \times 10^{-10}$

$K_a$  for  $HC_7H_5O_5$  is  $4.57 \times 10^{-3}$ , what is the  $K_b$  for  $NaC_7H_5O_5$ ?

A)  $4.57 \times 10^{-3}$  B)  $2.19 \times 10^{-12}$  C)  $4.53 \times 10^{-5}$  D)  $7.81 \times 10^{-6}$

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



The final results are

General relation

Between  $K_a$  and  $K_b$

$$K_{a1} \times K_{b2} = K_w$$

$$K_{a2} \times K_{b1} = K_w$$

And

$$K_{a1} \times K_{b3} = K_w$$

$$K_{a2} \times K_{b2} = K_w$$

$$K_{a3} \times K_{b1} = K_w$$

## 8.3 Weak-Acid Equilibria

### General Systematic Treatment of Equilibrium

- Unlike concentrated strong acid, need to account for water ionization
- Find pH for a solution of a general weak acid HA

How to find the pH of a solution of a weak acid HA, given its formal concentration F and its  $pK_a$ ?

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**Example: What is the pH of a 0.0500 M solution of o-hydroxybenzoic acid ( $K_a = 1.07 \times 10^{-3}$ )?**

**Step 1:** Pertinent reactions



**Step 2:** Charge Balance:  $[H^+] = [A^-] + [OH^-]$

**Step 3:** Mass Balance:

$$F = [HA] + [A^-] \quad F - \text{formal concentration of acid}$$

**Step 4:** Equilibrium constant expression (one for each reaction):

$$K_a = \frac{[A^-][H^+]}{[HA]} \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

**Step 5:** Count equations and unknowns:

**Four Unknowns** (1)  $[H^+] = [A^-] + [OH^-]$  (2)  $F = [HA] + [A^-]$  (3)  $K_a = \frac{[A^-][H^+]}{[HA]}$   
(4)  $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

**Four Unknowns:**  $[A^-], [HA], [H^+], [OH^-]$

**Step 6:** Solve (Not easy to solve  $\rightarrow$  cubic equation results!):

- Again, need to make assumptions to simplify equations
- The goal is to determine  $[H^+]$ , so we can measure pH

### Make Some Initial Assumptions:

- For a typical weak acid,  $[H^+]$  from HA will be much greater than  $[H^+]$  from  $H_2O$

If dissociation of HA is much greater than  $H_2O$ ,  $[H^+] \gg [OH^-]$

$$[H^+] = [OH^-] + [A^-] \Rightarrow [H^+] \approx [A^-]$$

Let  $[H^+] = x = [A^-]$ ;  $[HA] = F - x$

$$K_a = \frac{x^2}{F-x} \rightarrow x^2 + (K_a)x - (F)(K_a) = 0$$

Solve quadratic equation for x 
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 4(1)(F)(K_a)}}{2(1)} = [x^-]$$

### Step 7: Verify Assumption:

Was the approximation  $[H^+] \approx [A^-]$  justified ( $[H^+] \gg [OH^-]$ )?

Setting  $F = 0.050 \text{ M}$  and  $K_a = 1.07 \times 10^{-3}$  for *o*-hydroxybenzoic acid:

$$x = \frac{-K_a \pm \sqrt{K_a^2 + 4(1)(F)(K_a)}}{2(1)} = \frac{-1.07 \times 10^{-3} \pm \sqrt{(1.07 \times 10^{-3})^2 + 4(1)(0.0500)(1.07 \times 10^{-3})}}{2(1)}$$

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

$$pH = -\log x = 2.17$$

Determine  $[OH^-]$  from water dissociation

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{6.8 \times 10^{-3}} = 1.5 \times 10^{-12}$$

$[H^+] \gg [OH^-]$   
 $6.8 \times 10^{-3} \text{ M} \gg 1.5 \times 10^{-12} \text{ M}$   
*assumption is justified!*

## Fraction of Dissociation

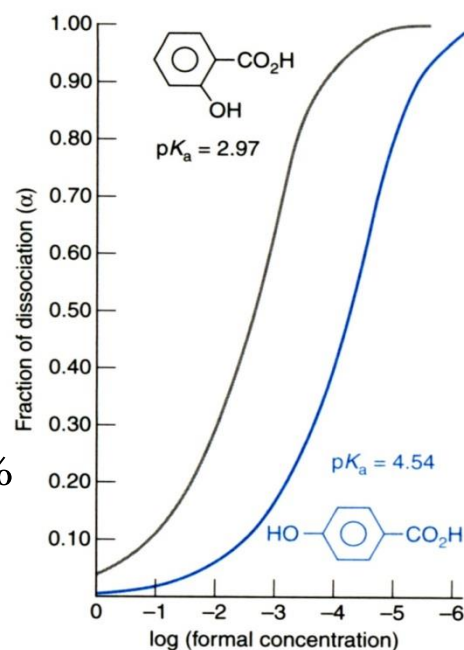
➤ Fraction of acid HA in the form  $A^-$  (a):

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

➤ Example:

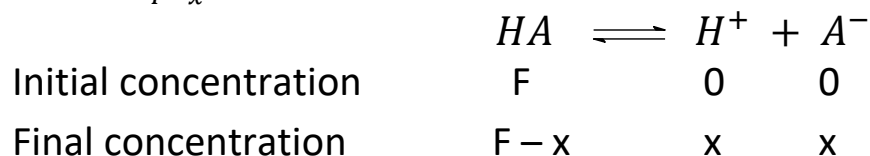
What is the percent fraction dissociation for  $F = 0.050\text{ M}$  and  $K_a = 1.07 \times 10^{-3}$  for *o*-hydroxybenzoic acid?

$$\alpha = \frac{x}{F} = \frac{6.8 \times 10^{-3}\text{ M}}{0.0500\text{ M}} = 0.14 = 14\%$$



➤ Percent dissociation increases with dilution

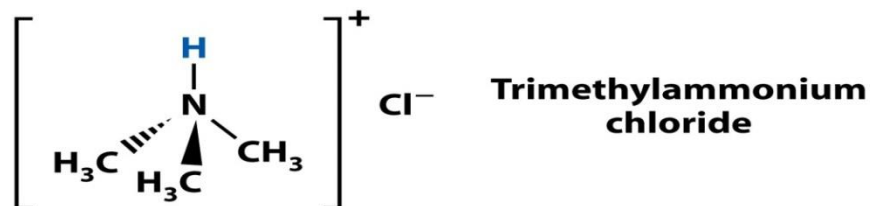
The expression  $K_a = \frac{x^2}{F-x}$  also follows from:



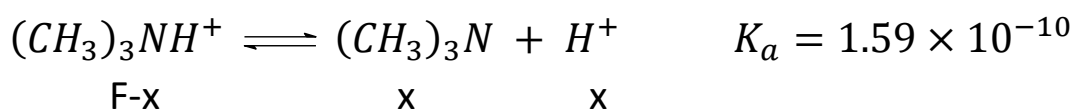
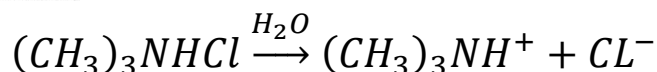
Alternative (easier) procedure: instead of solving the quadratic equation, you can at first neglect the  $x$  in the denominator, which in some cases will be small compared to  $F$  (i.e.  $< 1\%$  of  $F$ ):  $[H^+] = \sqrt{K_a \times F}$   
 Check that in the above example, however, this procedure is not allowed since  $\alpha (= \frac{7.31 \times 10^{-3}}{0.050} \times 100 = 14.6\%) > 1\%$  of  $F$ .



EXAMPLE 2: Find the pH of a 0.050 M trimethylammonium chloride



Unnumbered figure pg 165b  
Quantitative Chemical Analysis, Seventh Edition  
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$$\frac{x^2}{0.050 - x} = 1.59 \times 10^{-10}$$

Suppose  $0.050 - x \approx 0.050$

$$x = \sqrt{1.59 \times 10^{-10} \times 0.050} = 2.8 \times 10^{-6} M$$

$$\% \alpha = \frac{2.8 \times 10^{-6}}{0.050} \times 100 = 5.6 \times 10^{-3} \% \text{ which is less than } 1\% \text{ of } F \text{ (approximation is okay)}$$

$$pH = -\log 2.8 \times 10^{-6} = 5.55$$

## 8.4 Weak Base Equilibria

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Treatment of Weak Base is Very Similar to Weak Acid

➤ Assume all  $OH^-$  comes from base and not dissociation of water

**Step 1:** Pertinent reactions:



**Step 2:** Charge Balance:  $[H^+] + [BH^+] = [OH^-]$

**Step 3:** Mass Balance:

$$F = [B] + [BH^+] \Rightarrow [B] = F - [BH^+] \quad \text{F - formal concentration of base}$$

**Step 4:** Equilibrium constant expression (one for each reaction):

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

**Step 5:** Count equations (4) and unknowns (4)

➤ Assume all  $\text{OH}^-$  comes from base and not dissociation of water

**Step 6:** Solve (Assume  $[\text{BH}^+] \gg [\text{H}^+] \rightarrow [\text{BH}^+] \approx [\text{OH}^-]$ ):

$$[\text{BH}^+] = [\text{OH}^-] = x$$

$$[\text{B}] = F - x$$

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(x)(x)}{F - x} = \frac{x^2}{F - x}$$

Rearrange:

$$x^2 + (K_b)x - (F)(K_b) = 0$$

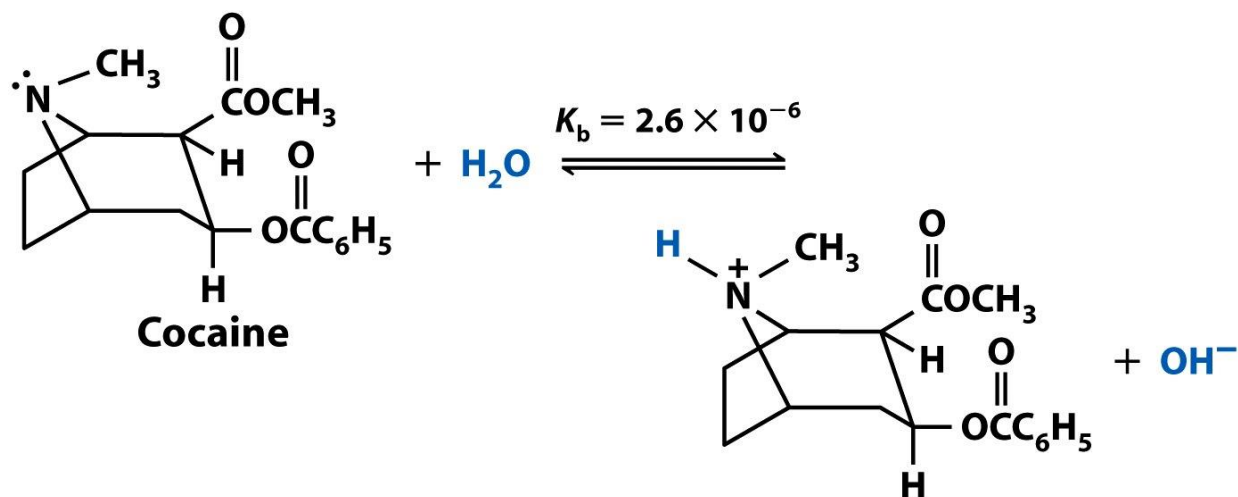
Solve quadratic equation:

$$x = \frac{-K_b \pm \sqrt{K_b^2 + 4(1)(F)(K_b)}}{2(1)} = [\text{OH}^-]$$

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Example

What is the pH of cocaine dissolved in water?  $F = 0.0372 \text{ M}$  and  $K_b = 2.6 \times 10^{-6}$  for cocaine?





$$\frac{x^2}{0.0372 - x} = 2.6 \times 10^{-6}$$

approximation  $\rightarrow \frac{x^2}{0.0372} = 2.6 \times 10^{-6} \rightarrow x = 3.1 \times 10^{-4} M$

Because  $x = [\text{OH}^-]$ , we need to solve for  $[\text{H}^+]$

$$[\text{H}^+] = K_w / [\text{OH}^-] = 1.0 \times 10^{-14} / 3.1 \times 10^{-4} = 3.2 \times 10^{-11}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(3.2 \times 10^{-11}) = 10.49$$

### Fraction of Association

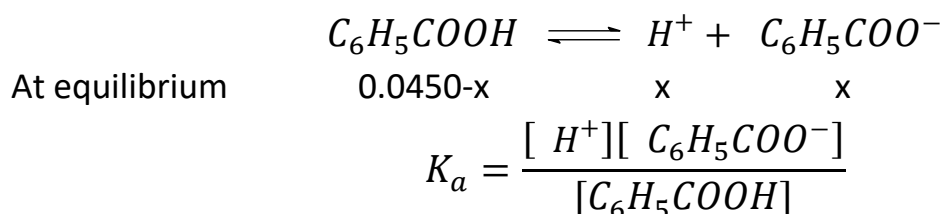
➤ Fraction of Base B in  $\text{BH}^+$  form (a):

$$\alpha = \frac{[\text{BH}^+]}{[\text{BH}^+] + [\text{B}]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

What is the percent fraction dissociation of cocaine reacted with water?  $F = 0.0372 M$  and  $K_b = 2.6 \times 10^{-6}$  for cocaine?

$$\alpha = \frac{x}{F} = \frac{3.1 \times 10^{-4} M}{0.0372 M} = 0.0083 = 0.83\%$$

A 0.0450 M solution of benzoic acid has a pH of 2.78. Calculate  $\text{p}K_a$  for this acid. What is the percent fraction dissociation?



$$\text{pH} = -\log[\text{H}^+] \rightarrow 2.78 = -\log[\text{H}^+] \rightarrow [\text{H}^+] = 1.7 \times 10^{-3} M = [\text{C}_6\text{H}_5\text{COO}^-]$$

$$\alpha = 3.8\%$$

## Conjugate Acids and Bases- Revisted

Isomer of hydroxybenzoic acid	$K_a$	$K_b = K_w/K_a$
Ortho	$1.07 \times 10^{-3}$	$9.3 \times 10^{-12}$
para	$2.9 \times 10^{-5}$	$3.5 \times 10^{-10}$

pH of 0.050 M o-hydroxybenzoate = 7.83

pH of 0.050 M p-hydroxybenzoate = 8.62

**The conjugate base of the stronger acid is the weaker base.**

Example: Find the pH of 0.10 M ammonia.

In Appendix G, we find ammonium ion, listed next to ammonia.  $pK_a$  for ammonium ion is 9.245. Therefore,  $K_b$  for  $NH_3$  is

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14.00}}{10^{-9.245}} = 1.76 \times 10^{-5}$$

	$NH_3$	+	$H_2O$	$\rightleftharpoons$	$NH_4^+$	+	$OH^-$
Initially	0.10				0		0
At Equilibrium	$0.10 - x$		-		x		x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.76 \times 10^{-5}$$

$$1.76 \times 10^{-5} = \frac{x^2}{0.10 - x}$$

$$(1.8 \times 10^{-5})(0.10) = x^2$$

$$2.7 \times 10^{-6} = x^2$$

$$x = [OH^-] = 1.33 \times 10^{-3}$$

Therefore,

$$pOH = -\log(1.33 \times 10^{-3})$$

$$pOH = 2.88$$

$$pH = 14.00 - 2.88 = 11.12$$

Test Yourself Find the pH of 0.10 M methylamine. (Answer: 11.80)

Q1) A 0.020 M solution of niacin has a pH 3.26. Calculate the percent ionization of the niacin. Dr. Rjoob

Answer: 2.7%

Q2) What is the pH of a 0.122M monoprotic acid whose  $K_a$  is  $5.7 \times 10^{-4}$ ?

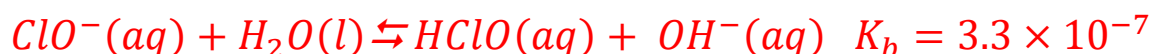
Answer: 0.0083 M

Q3)  $K_a$  for HClO is  $3.0 \times 10^{-8}$ . What is the pH at 25°C of aqueous solution that is 0.020 M in HClO? Dr. Rjoob

Q4) Find the pH of 0.10 M ammonia ( $\text{NH}_3$ ,  $K_b = 1.76 \times 10^{-5}$ )

Answer: 11.12

Q5) A solution made by adding solid NaClO to enough water to make 2.00 L of solution has a pH of 10.50. Calculate the number of moles of NaClO that were added to water.



Answer: 0.62

Q6) A solution of  $\text{NH}_3$  ( $K_b = 1.8 \times 10^{-5}$ ) in water has a pH of 11.17. What is the molarity of the solution?

Answer: 0.12 M

Q7) What is the percent of ionization of HClO in a 0.015 M solution of HClO?  $K_a = 3.0 \times 10^{-8}$

A)  $4.5 \times 10^{-8}$       B) 14      C)  $2.1 \times 10^{-5}$       D) 0.14

Q8) The  $\text{p}K_a$  value for the conjugate acid of the base quinolone is 4.90. Calculate the base-dissociation constant of quinolone.

Answer:  $7.9 \times 10^{-10}$ .

Q9)  $K_a$  for  $\text{HC}_7\text{H}_5\text{O}_5$  is  $4.57 \times 10^{-3}$ , what is the  $K_b$  for  $\text{NaC}_7\text{H}_5\text{O}_5$ ?

A)  $4.57 \times 10^{-3}$     B)  $2.19 \times 10^{-12}$     C)  $4.53 \times 10^{-5}$     D)  $7.81 \times 10^{-6}$

Q10) The  $K_a$  for HCN is  $4.9 \times 10^{-10}$ . What is the pH of 0.30 M NaCN solution?

Q11) (a) Given that  $K_a$  for acetic acid ( $\text{CH}_3\text{COOH}$ ) is  $1.8 \times 10^{-5}$  and that for hypochlorous acid ( $\text{HClO}$ ) is  $3.0 \times 10^{-8}$ , which is the stronger acid? (b) Which is the stronger base, the acetate ion or the hypochlorite ion? (c) Calculate  $K_b$  values for  $\text{CH}_3\text{COO}^-$  and  $\text{ClO}^-$ .

Q12) Calculate the  $K_a$  for an unknown monoprotic acid HX, given that a solution of 0.10 M LiX has a pH of 8.90.

A)  $7.9 \times 10^{-6}$     B)  $4.3 \times 10^{-8}$     C)  $6.2 \times 10^{-10}$     D)  $1.6 \times 10^{-5}$

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## 8.5 Buffers

A buffered solution resists changes in pH when acids or bases are added or when dilution occurs.

A **buffer solution** is a solution of:

1. A weak acid with its conjugate base

Examples:  $\text{HF}/\text{NaF}$ ;  $\text{HCOOH}/\text{HCOONa}$ ;  $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$

2. A weak acid (excess) with a strong base

Example:  $\text{HF}/\text{NaOH}$ ,  $\text{HCN}/\text{KOH}$

3. A weak base with its conjugate acid

Example:  $\text{NH}_3/\text{NH}_4\text{Cl}$

4. A weak base (excess) with a strong acid

Example:  $\text{NH}_3/\text{HBr}$

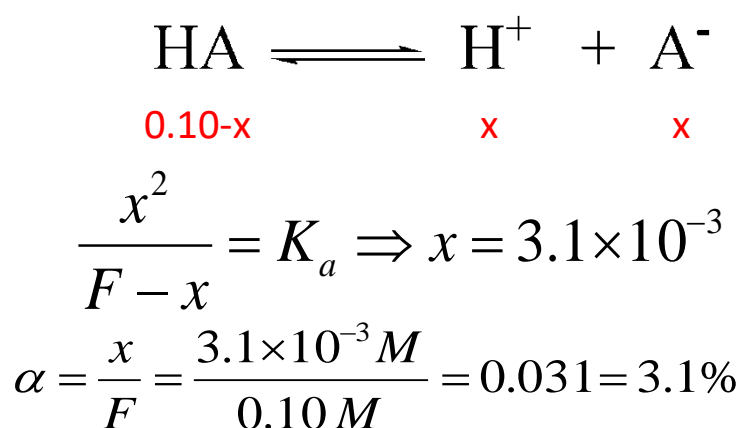
- **Must be comparable amounts of acid & base**

Which of the following are buffer systems? (a) KF/HF(b) KBr/HBr, (c)  $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ , (d)  $\text{Na}_2\text{CO}_3/\text{H}_2\text{CO}_3$

- For an organism to survive, it must control the pH of each subcellular compartments
  - **Enzyme-catalyzed reactions are pH dependent**

Mixing a Weak Acid and Its Conjugated Base

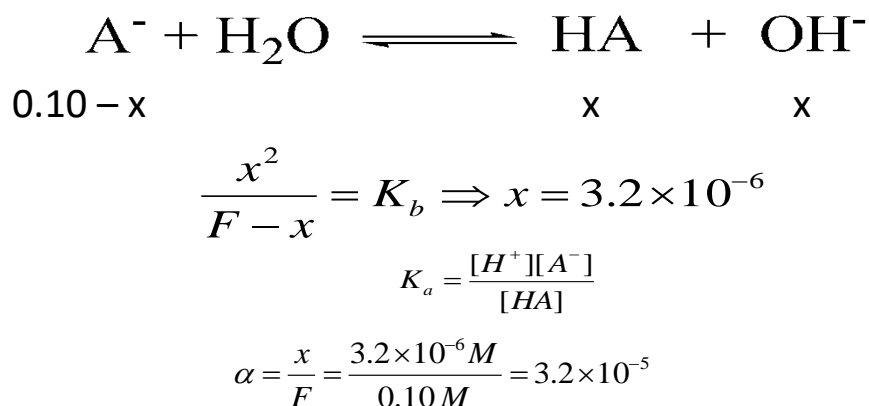
- Very little reaction occurs
- Very little change in concentrations
- Example:
- Consider a 0.10 M of acid with  $\text{pK}_a$  of 4.00



➤ Example:

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- Consider adding 0.10 M of conjugate base with  $\text{pK}_b$  of 10.00



*HA dissociates very little and  $\text{A}^-$  reacts very little with water*

## Henderson-Hasselbalch Equation

- Rearranged form of  $K_a$  equilibrium equation:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Take log of both sides:

$$\log K_a = \log \frac{[H^+][A^-]}{[HA]} = \log[H^+] + \log \frac{[A^-]}{[HA]}$$

rearrange:

$$-\log[H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)$$

$$pH = pK_a + \log \frac{[A^-]\gamma_{A^-}}{[HA]\gamma_{HA}}$$

## Henderson-Hasselbalch Equation

- Determines pH of buffered solution
- **Need to know ratio of conjugate [acid] and [base]**

$$pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right)$$

- If  $[A^-] = [HA]$ ,  $pH = pK_a$ 
  - ***All equilibria must be satisfied simultaneously in any solution at equilibrium***
- **Only one concentration of  $H^+$  in a solution**

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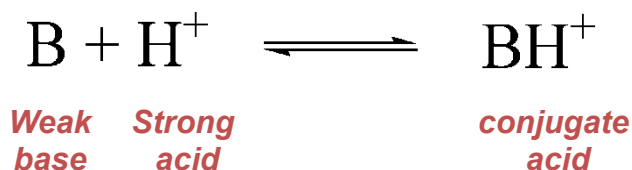


- Similar equation for weak base and conjugate acid

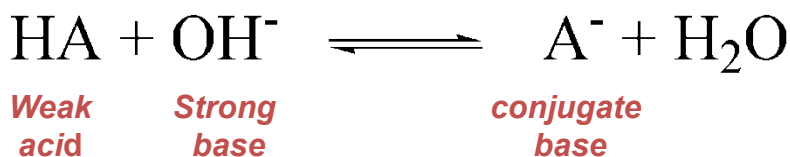
$$pH = pK_a + \log \left( \frac{[B]}{[BH^+]} \right) \quad \text{pK}_a \text{ is for this acid}$$

$[A^-]/[HA]$	pH
100:1	$pK_a + 2$
10:1	$pK_a + 1$
1:1	$pK_a$
1:10	$pK_a - 1$
1:100	$pK_a - 2$

- A strong acid and a weak base react “completely” to give the conjugate acid:



- Also, a strong base and a weak acid react “completely” to give the conjugate base:



Example: What is the  $pH$  of a solution containing  $0.30\text{ M HCOOH}$  ( $K_a = 1.7 \times 10^{-4}$ ) and  $0.52\text{ M HCOOK}$ ?

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

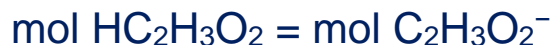
$$pK_a = -\log K_a = -\log 1.7 \times 10^{-4} = 3.77$$

$$pH = 3.77 + \log \frac{(0.52)}{(0.30)} = 3.77 + 0.24 = 4.01$$

A buffer is made by adding 0.300 mol  $\text{HC}_2\text{H}_3\text{O}_2$  and 0.300 mol  $\text{NaC}_2\text{H}_3\text{O}_2$  to enough water to make 1.00 L of solution. The  $\text{pH}$  of the buffer is 4.74. Calculate the  $\text{pH}$  of this solution after 0.020 mol of  $\text{NaOH}$  is added.

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Before the reaction, since



$$\text{pH} = \text{pK}_a = -\log (1.8 \times 10^{-5}) = 4.74$$

The 0.020 mol  $\text{NaOH}$  will react with 0.020 mol of the acetic acid:



	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	$\text{OH}^-$
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction	0.280 mol	0.320 mol	0.000 mol

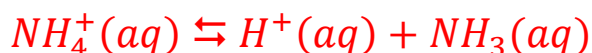
$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = 4.74 + \log \frac{[0.32]}{[0.28]}$$

$$\text{pH} = 4.74 + 0.06 = 4.80$$

$$\Delta\text{pH} = 4.80 - 4.74 = 0.06$$

Calculate the  $pH$  of the  $0.30\text{ M NH}_3/0.36\text{ M NH}_4\text{Cl}$  buffer system. What is the  $pH$  after the addition of  $20.0\text{ mL}$  of  $0.050\text{ M NaOH}$  to  $80.0\text{ mL}$  of the buffer solution?  $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$



Before the reaction:

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

$$pK_b = -\log K_b = -\log 1.8 \times 10^{-5} = 4.74$$

$$pK_a + pK_b = 14.00$$

$$pK_a = 14.00 - 4.74 = 9.26$$

$$pH = 9.26 + \log \frac{[0.30]}{[0.36]} = 9.26 - 0.08 = 9.18$$

After the reaction:

$$\text{Moles of NaOH added} = 0.020 \times 0.050 = 0.0010$$

$$\text{Moles of NH}_4^+ = 0.080 \times 0.36 = 0.029$$

$$\text{Moles of NH}_3 = 0.080 \times 0.30 = 0.024$$

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$$\text{Start moles: } 0.029 \quad 0.0010 \quad 0.024$$



$$\text{End moles: } 0.028 \quad 0.00 \quad 0.025$$

$$[\text{NH}_4^+] = \frac{0.028}{0.10} = 0.0028\text{ M}$$

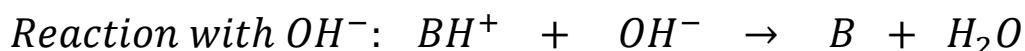
$$[\text{NH}_3] = \frac{0.025}{0.10} = 0.0025\text{ M}$$

$$pH = 9.26 + \log \frac{[0.0025]}{[0.0028]} = 9.26 - 0.05 = 9.21$$

## Calculating How to Prepare a Buffer Solution

How many milliliters of 0.500 M NaOH should be added to 10.0 g of tris hydrochloride ( $pK_a = 8.072$ ) to give a pH of 7.60 in a final volume of 250 mL?

Solution The moles of tris hydrochloride are  $(10.0 \text{ g})/(157.596 \text{ g/mol}) = 0.0635 \text{ mol}$ . We can make a table to help solve the problem:



Initial moles	0.0635	$x$	—
---------------	--------	-----	---

Final moles	$0.0635 - x$	—	$x$
-------------	--------------	---	-----

The Henderson-Hasselbalch equation allows us to find  $x$ , because we know pH and

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$$pH = pK_a + \log \frac{\text{mol } B}{\text{mol } BH^+}$$

$$7.60 = 8.072 + \log \frac{x}{0.0635}$$

$$-0.472 = \log \frac{x}{0.0635 - x}$$

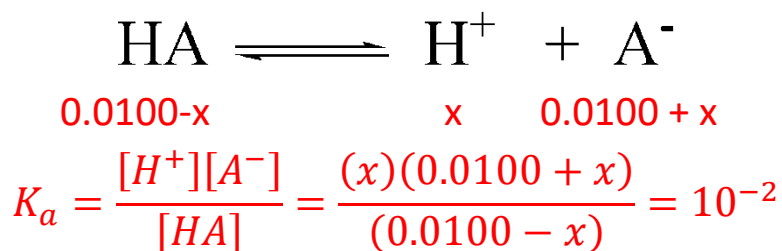
$$x = 0.0160 \text{ mol}$$

This many moles of NaOH is contained in

$$\frac{0.0160 \text{ mol}}{0.500 \text{ mol/L}} = 0.0320 \text{ L} = 32.0 \text{ mL}$$

How many mL of 0.500 M NaOH should be added to 10.0 g of tris hydrochloride to give a pH of 7.40 in a final volume of 500 mL?  
(**Answer:** 22.3 mL)

What will the pH if 0.0100 mol of HA ( $pK_a = 2.00$ ) and 0.010 mol of  $A^-$  are dissolved in water to make 1.00 L of solution?



$$\rightarrow x = 0.00414 \text{ M} \rightarrow \text{pH} = 2.38$$

The concentrations of HA and  $A^-$  are not what mixed.

$$[\text{HA}] = F_{\text{HA}} - [\text{H}^+] = 0.0100 - 0.00414 = 0.00586 \text{ M}$$

$$[\text{A}^-] = F_{\text{A}^-} + [\text{H}^+] = 0.0100 + 0.00414 = 0.0141 \text{ M}$$

### Preparing a Buffer in Real Life!

If you really wanted to prepare a tris buffer of pH 7.60, you would *not* do it by calculating what to mix.

Suppose that you wish to prepare 1.00 L of buffer containing 0.100 M tris at a pH of 7.60. You have available solid tris hydrochloride and approximately 1 M NaOH. Here's how I would do it:

1. Weigh out 0.100 mol of tris hydrochloride and dissolve it in a beaker containing about 800 mL of water.
2. Place a calibrated pH electrode in the solution and monitor the pH.
3. Add NaOH solution until the pH is exactly 7.60.
4. Transfer the solution to a volumetric flask and wash the beaker a few times. Add the washings to the volumetric flask.
5. Dilute to the mark and mix.

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You do not simply add the calculated quantity of NaOH because it would not give exactly the desired pH.

The reason for using 800 mL of water in the first step is so that the volume will be reasonably close to the final volume during pH adjustment. Otherwise, the pH will change slightly when the sample is diluted to its final volume and the ionic strength changes.

## Buffer Capacity

- A Buffer resists changes in pH because strong acid or base is consumed by B or BH<sup>+</sup>

**Buffer capacity**,  $\beta$ , is a measure of how well a solution resists changes in pH when strong acid or base is added. Buffer capacity is defined as

$$\beta = \frac{dC_b}{dpH} = -\frac{dC_a}{dpH}$$

Where  $C_a$  and  $C_b$  are the number of moles of strong acid and strong base per liter needed to produce a unit change in pH. The greater the buffer capacity, the more resistant the solution is to pH change.

Buffer capacity reaches a maximum when  $pH = pK_a$ . That is, *a buffer is most effective in resisting changes in pH when  $pH = pK_a$*  (that is, when  $[HA] = [A^-]$ ).

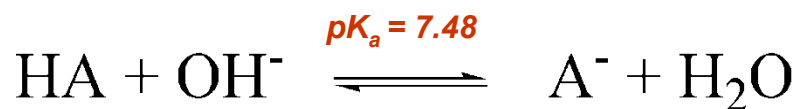
Dr. Rjoob

### Choosing a Buffer

- Choose a buffer with  $pK_a$  as close as possible to desired pH
- Useful buffer range is  $pK_a \pm 1 \text{ pH units}$
- Outside this range, there is not enough of either the weak acid or the weak base to react with added base or acid.
- Buffer pH depends on temperature and ionic strength → activity coefficients

**Buffer capacity** can be *increased* by *increasing* **the concentration of the buffer**.

Calculate how many milliliters of 0.626 M KOH should be added to 5.00 g of MOBS (223.29 g/mol) to give a pH of 7.40?



What is the pH if an additional 5 mL of the KOH solution is added?

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