Acids and Bases

Review: Petrucci et al. Chapter 5, section 5-3.

Reading: from chapter 16 of Petrucci et al.

***Required*:** Sections 16-1 through 16-5, 16-7.

***Recommended*:** Sections 16-8 and 16-9.

***Examples*:**16-1 through 16-6, 16-10 through 16-13.

Assigned problems: Chapter 16 questions 2, 9, 10, 24, 25, 27, 56, 57a-d, 61, 112

Properties of Acids and Bases

Acids are a group of compounds with certain common properties:

- sour taste
- dissolve carbonates with release of CO_2
- dissolve metals with release of H_2
- acids contain hydrogen (except for some *Lewis acids*)

Bases also have certain common properties:

- bitter taste
- slippery feel

Acids and bases neutralize each other.

Arrhenius Theory of Acids and Bases

Section 16.1

Acids are substances that produce hydrogen ions, **H^+**, in solution.

Bases are substances that produce hydroxide ions, **OH^-**, in solution.

Neutralization: $H^+ + OH^- \rightarrow H_2O$

Shortcomings:

- Only works in water.
- Can be clumsy to identify acids and bases. Example:

$$NH_3 + HCHO_2 \leftrightharpoons NH_4^+ + CHO_2^-$$

The Hydrogen Ion in Solution

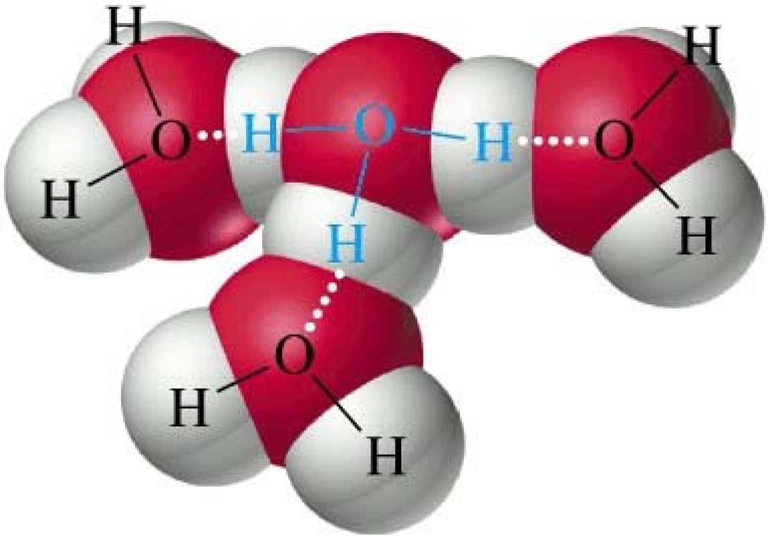
H^+ is a *bare proton*.

- very concentrated charge
- *interacts strongly* with other molecules

In water, H^+ forms the **hydronium ion**, H_3O^+.

- H_3O^+ is usually hydrated by three water molecules.
- We can use *either* H^+ or H_3O^+ in equations.

Hydronium ion
H_3O^+



A hydrated proton
$H_9O_4^+$

Bronsted-Lowry Theory - Section 16.2

An **acid** is a **proton donor** (that is, a H^+ donor).

A **base** is a **proton acceptor**.

Examples:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

acid base

$$H_2O + H_2O \rightarrow H_3O^+ + OH^-$$

acid base

$$NH_3 + HCHO_2 \leftrightharpoons NH_4^+ + CHO_2^-$$

base acid acid base

More general than Arrhenius; gives same results in H_2O.

Amphiprotic Substances

Amphiprotic substances can act as ***either*** an acid or a base.

Examples:

$H_2O + H_2O \rightarrow H_3O^+ + OH^-$

H_2O is both an acid and a base.

$H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

$H_2PO_4^-$ is an acid.

$H_2PO_4^- + H_2O \rightarrow H_3PO_4 + OH^-$

$H_2PO_4^-$ is a base.

H_2O and $H_2PO_4^-$ are amphiprotic species.

Conjugate Pairs of Acids and Bases

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

Acids and bases come in *pairs*. The acid has one more H^+ than the base.

- NH_3 and NH_4^+ are a **conjugate pair**.
  - NH_4^+ is the **conjugate acid** of NH_3.
  - NH_3 is the **conjugate base** of NH_4^+.
- H_2O and OH^- are another conjugate pair.
  - H_2O is the **conjugate acid** of OH^-.
  - OH^- is the **conjugate base** of H_2O.

Identifying Conjugate Acids and Bases

Which is the conjugate base of HPO_4^{2-}?

a) OH^-

b) $H_2PO_4^-$

c) PO_4^{3-}

Which is the conjugate acid of HSO_4^-?

a) H_3O^+

b) H_2SO_4

c) SO_4^{2-}

Base Ionization Constant

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Ammonia, NH_3, acts as a base in this reaction.

The equilibrium constant for the transfer of one proton from the solvent to a base is called the **base ionization constant**, K_b.

For NH_3 in water at 25 °C:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5}$$

$[H_2O]$ does not appear in K_b since water is the solvent.

The value of K_b depends on the base, the solvent, and the temperature.

Acid Ionization Constant

$$CH_3CO_2H(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

Acetic acid, CH_3CO_2H, acts as an acid in this reaction.

The equilibrium constant for the transfer of one proton from an acid to the solvent is called the **acid ionization constant**, K_a.

For CH_3CO_2H in water:

$$K_a = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

$[H_2O]$ does not appear in K_a since water is the solvent.

The value of K_a depends on the acid, the solvent, and the temperature.

Identifying Ionization Constants

For which reaction is the equilibrium constant a K_b?

a) $H_2PO_4^- + H_2O \leftrightharpoons HPO_4^{2-} + H_3O^+$

b) $H_2PO_4^- + OH^- \leftrightharpoons HPO_4^{2-} + H_2O$

c) $H_2PO_4^- + H_2O \leftrightharpoons H_3PO_4 + OH^-$

For which of the above reactions is the equilibrium constant a K_a?

Self-Ionization - Section 16.3

$$H_2O(l) + H_2O(l) \leftrightharpoons H_3O^+(aq) + OH^-(aq)$$

Water acts as both an acid and a base in this reaction.

The equilibrium constant for the transfer of a proton from the solvent to the solvent is called the **self-ionization constant**.

For water at 25 °C: $K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

K_W is also called the *ion product* or the *autoionization constant*.

Consequences:

- H_3O^+ and OH^- are always present in water.
- There is a fixed relation between $[H_3O^+]$ and $[OH^-]$: higher $[H_3O^+]$ means lower $[OH^-]$ and vice-versa.

K_a and K_b for Conjugate Pairs

Acid: $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ $K_a = [H_3O^+][NH_3]/[NH_4^+]$

Base: $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K_b = [NH_4^+][OH^-]/[NH_3]$

Solvent: $2H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_W = [H_3O^+][OH^-]$

$$\mathbf{K_a \times K_b = K_W}$$

For any ***conjugate pair***:

- The sum of the acid and base ionization reactions equals the self-ionization reaction for the solvent (water).
- *The product of the acid and base ionization constants equals the self-ionization constant for the solvent (water)*.

Example: For NH_3, $K_b = 1.8 \times 10^{-5}$, so for NH_4^+, $K_a = 5.6 \times 10^{-10}$.

Self-Ionization of Water

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

For water at 25 °C: $K_W = [H_3O^+][OH^-] = 1.0\times10^{-14}$

- In pure water, $[H_3O^+] = [OH^-] = 1.0\times10^{-7}$ M
- The minimum concentration of ions in water is 2.0×10^{-7} M.
- If $[H_3O^+] > 1.0\times10^{-7}$ M, then $[OH^-] < 1.0\times10^{-7}$ M, such a solution is ***more acidic*** than pure water.
- If $[H_3O^+] < 1.0\times10^{-7}$ M, then $[OH^-] > 1.0\times10^{-7}$ M, such a solution is ***more basic*** than pure water.
- Concentrations of H_3O^+ and OH^- can cover a huge range.

The pH Scale

Used to measure the acidity of aqueous solutions. The logarithmic scale covers a wide range of concentrations.

pH (potential of hydrogen ion) is defined as the negative of the base-ten logarithm of the hydrogen ion concentration:

$$\mathbf{pH = -log[H_3O^+]}$$

- For pure water at 25 °C: $[H_3O^+] = 1.0\times10^{-7}$ M,

  so **pH = 7.00**. This is a **neutral** solution.
- In **acidic** solutions, $[H_3O^+] > 1.0\times10^{-7}$ M, so **pH < 7.00**.
- In **basic** solutions, $[H_3O^+] < 1.0\times10^{-7}$ M, so **pH > 7.00**.

pOH and pK_W

pOH is defined as the negative logarithm of the hydroxide ion concentration:

$$\mathbf{pOH = -log[OH^-]}$$

pK_W is defined as the negative logarithm of the self-ionization constant of water:

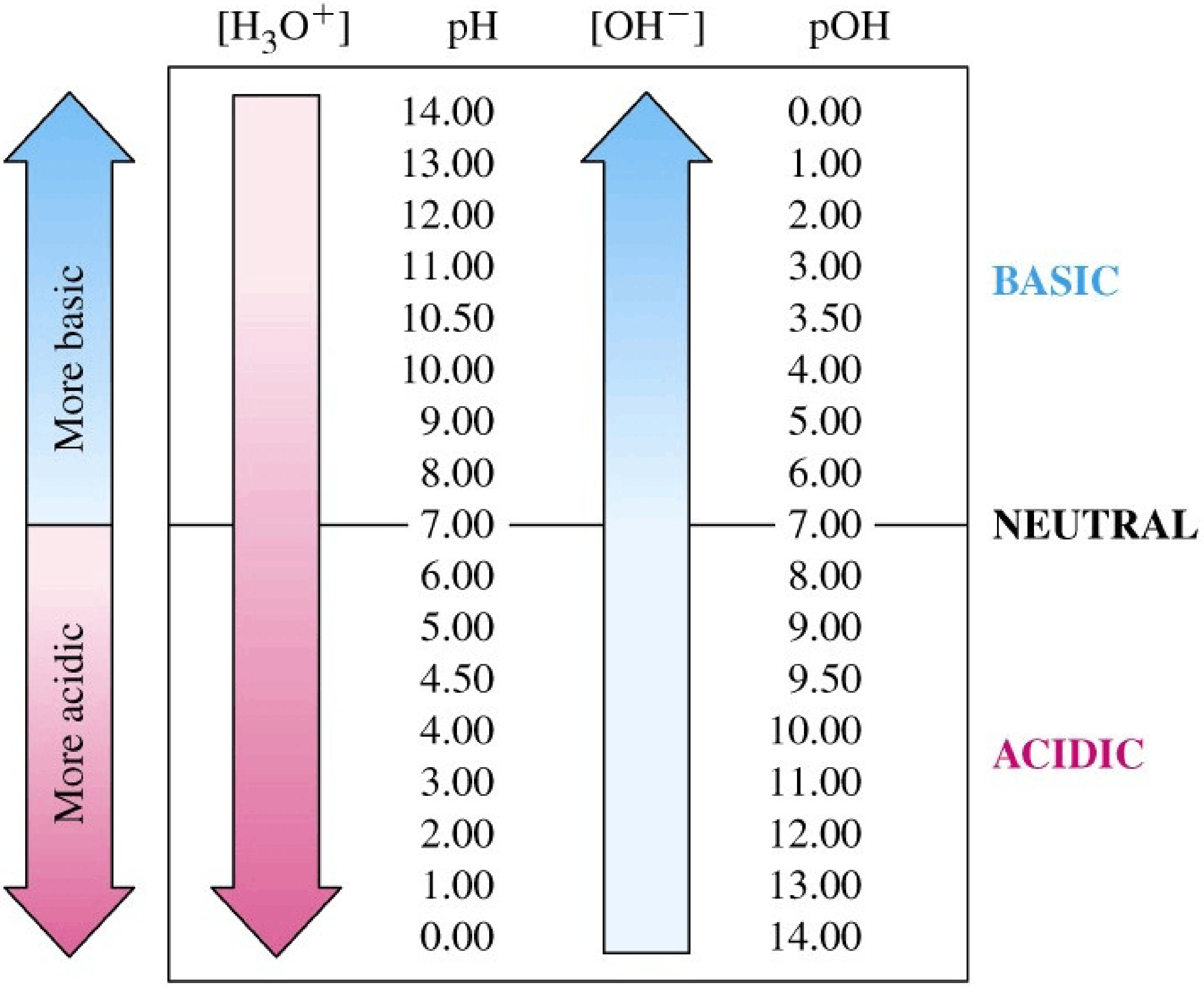
$$\mathbf{p}K_W = -\mathbf{log}(K_W)$$

Since $K_W = [H_3O^+][OH^-] = 1.0\times10^{-14}$

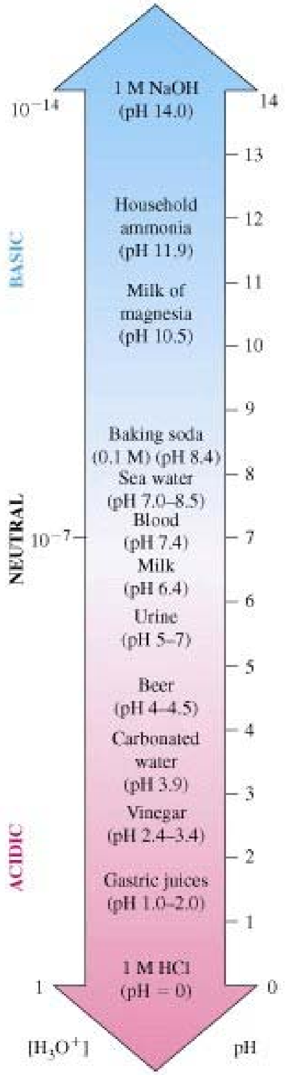
$$-\log(K_W) = -\log[H_3O^+] - \log[OH^-] = -\log(1.0\times10^{-14})$$

$\therefore \quad \mathbf{p}K_W = \mathbf{pH + pOH} = 14.00$

pH and pOH



$[H_3O^+]$	pH	$[OH^-]$	pOH
	14.00		0.00
	13.00		1.00
	12.00		2.00
	11.00		3.00
	10.50		3.50
	10.00		4.00
	9.00		5.00
	8.00		6.00
	7.00		7.00
	6.00		8.00
	5.00		9.00
	4.50		9.50
	4.00		10.00
	3.00		11.00
	2.00		12.00
	1.00		13.00
	0.00		14.00



Interpreting pH and pOH

For each of the following, identify whether the solution is

a) acidic
b) neutral
c) basic

(1) pH = 9.55

(2) pOH = 8.52

(3) pH = 7.00

(4) pOH = 3.58

pK_a and pK_b

pK_a is defined as the negative logarithm of an acid ionization constant:

$$\mathbf{pK_a = -\log(K_a)}$$

Example: $NH_4^+ + H_2O \leftrightharpoons H_3O^+ + NH_3 \; K_a = 5.6\times10^{-10}$

$$\Rightarrow \; pK_a = -\log(5.6\times10^{-10}) = 9.25$$

pK_b is defined as the negative logarithm of a base ionization constant:

$$\mathbf{pK_b = -\log(K_b)}$$

Example: $NH_3 + H_2O \leftrightharpoons NH_4^+ + OH^- \;\; K_b = 1.8\times10^{-5}$

$$\Rightarrow \; pK_b = -\log(1.8\times10^{-5}) = 4.75$$

Note that $pK_a + pK_b = 14.00$ for a conjugate pair in water.

Strong Acids and Bases

Strong acids and bases ionize almost completely in water at ordinary pHs ($0 < pH < 14$).

Common strong acids:
hydrogen halides (except HF) and some oxyacids.

Common strong bases: hydroxides of the alkali metals and alkaline earths.

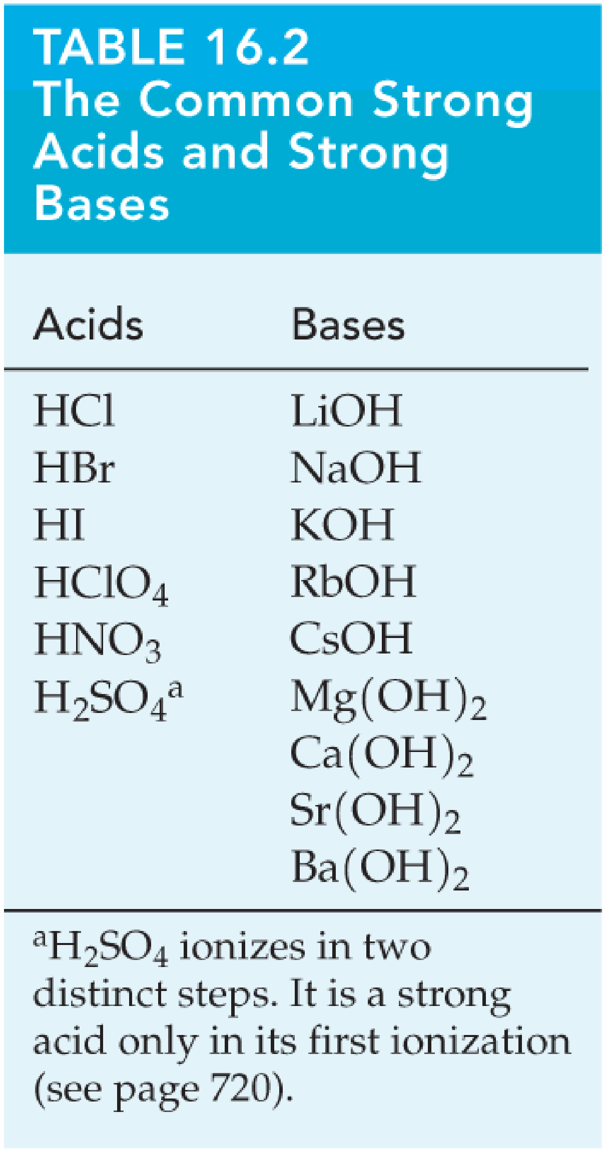


TABLE 16.2
The Common Strong Acids and Strong Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4[a]	$Mg(OH)_2$
	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

[a] H_2SO_4 ionizes in two distinct steps. It is a strong acid only in its first ionization (see page 720).

Conjugates of Strong Acids and Bases

Cl^-, Br^-, NO_3^- are the conjugate bases of HCl, HBr, HNO_3. Do salts of these anions make a solution basic?

For a conjugate pair, **$pK_a + pK_b = 14.00$**.

For a strong acid, $pK_a < 0$. So for its conjugate base, $pK_b > 14$. The base is too weak to matter in water.

∴ The conjugate bases of strong acids are essentially 'pH neutral' in water.

Note: The conjugate acid of a hydroxide (LiOH, $Ca(OH)_2$, ...) is water.

pH of a Strong Acid (or Base) Solution

Find pH and pOH for a 0.010 M solution of HNO_3.

$$HNO_3 + H_2O \leftrightharpoons H_3O^+ + NO_3^-$$

Solution: Assume complete ionization. The solution is 0.010 M in both NO_3^- and H_3O^+.

$[H_3O^+] = 0.010\ M = 1.0\times10^{-2}\ M \quad \Rightarrow \quad pH = 2.00$

$pOH = 14.00 - pH = 12.00 \quad \Rightarrow \quad [OH^-] = 1.0\times10^{-12}\ M$

Watch out: This only works if $[H_3O^+]$ is much greater than 1.0×10^{-7} M.

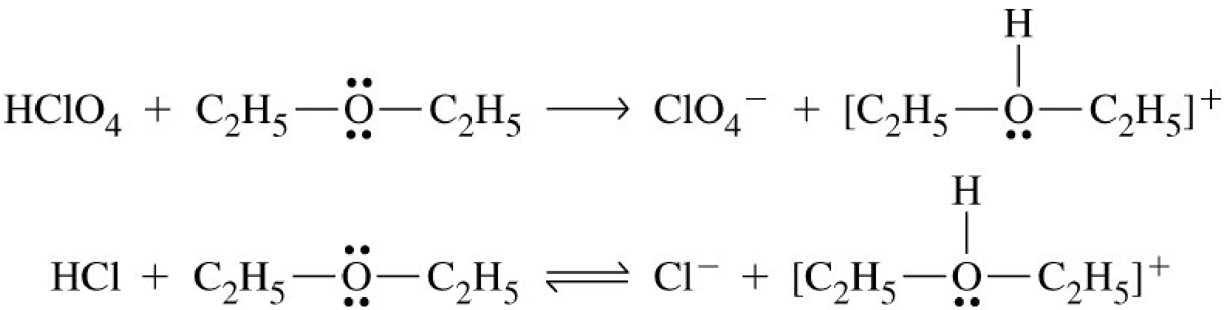
Use reasoning above: What is the pH of a 1.0×10^{-8} M solution of HNO_3? pH = 8.00. ***Obviously wrong, see later*!**

Non-aqueous Solvents

$HClO_4$, HI, HBr, HCl, H_2SO_4 and HNO_3 are strong acids.

In water, we can not tell which is stronger – they all ionize completely.

Strong acids can be differentiated by using a solvent that is a weaker base than water.



$$HClO_4 + C_2H_5{-}\ddot{\underset{\cdot\cdot}{O}}{-}C_2H_5 \longrightarrow ClO_4^- + [C_2H_5{-}\underset{\cdot\cdot}{\overset{H}{\overset{|}{O}}}{-}C_2H_5]^+$$

$$HCl + C_2H_5{-}\ddot{\underset{\cdot\cdot}{O}}{-}C_2H_5 \rightleftharpoons Cl^- + [C_2H_5{-}\underset{\cdot\cdot}{\overset{H}{\overset{|}{O}}}{-}C_2H_5]^+$$

In diethylether,$HClO_4$ ionizes completely. It is a stronger acid than HCl.

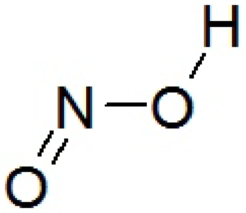
Weak Acids and Bases

Weak acids and bases are usually partially ionized in water at ordinary pHs ($0 < pH < 14$).

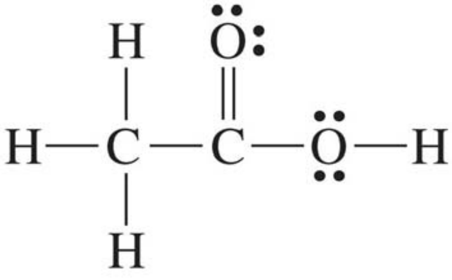
Some weak acids

($0 < pK_a < 14$)

HF, HOCl, HNO_2, carboxylic acids.



nitrous acid K_a = 7.2×10^{-4}



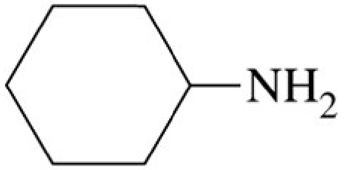
acetic acid

$K_a = 1.8 \times 10^{-5}$

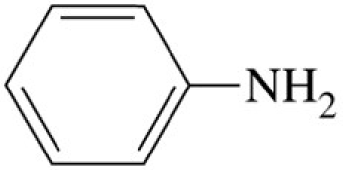
Some weak bases

($0 < pK_b < 14$)

NH_3, amines, aniline



Cyclohexylamine, $pK_b = 3.36$



Aniline, $pK_b = 9.13$

Relative Strengths of Acids and Bases

The **strength** of an **acid** is determined by its **pK_a**.

- lower pK_a ⇒ stronger acid
- higher pK_a ⇒ weaker acid

The **strength** of a **base** is determined by its **pK_b**.

- lower pK_b ⇒ stronger base
- higher pK_b ⇒ weaker base

For a conjugate pair, $pK_a + pK_b = 14.00$. So

- The stronger an acid, the weaker its conjugate base.
- The stronger a base, the weaker its conjugate acid.

Conjugates of Weak Acids and Bases

The conjugate base of a weak acid is

a) a strong base

b) a weak base

c) pH neutral (no effect on pH)

Acid-Base Concepts - Summary

- An acid is a proton donor; a base is a proton acceptor.
- Some substances can be both an acid and a base.
- Acids and bases come in conjugate pairs.
- Stronger acid ⇒ weak conjugate base and vice-versa.
- Water self-ionizes to form H_3O^+ and OH^-.
- Acidity is measured on the pH scale: $\mathrm{pH} = -\log[H_3O^+]$
- pK_a and pK_b describe the strengths of acids and bases.
- Strong acids and bases ionize almost completely; weak acids and bases partially ionize.

Acid-Base Equilibrium Calculations

pH is a critical parameter for many chemical reactions.

Acids (and bases) often react very differently from their conjugate bases (and acids).

In doing equilibrium calculations:

- Identify the ***important*** species and reactions.
- Make use of ***mass balance*** and ***equilibrium constants*** (ICE table).
- Think about what a ***reasonable answer*** would be.
- Make ***simplifying assumptions***, if possible.

K_a of a Weak Acid from Solution pH

A 0.150 M solution of HOCl has pH = 4.18. **Find K_a.**

Solution:

$$\mathrm{HOCl + H_2O \leftrightharpoons H_3O^+ + OCl^-}$$

$$K_a = [\mathrm{H_3O^+}]\,[\mathrm{OCl^-}] \,/\, [\mathrm{HOCl}]$$

If this is the only reaction, we must have $[\mathrm{H_3O^+}] = [\mathrm{OCl^-}]$.

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \Rightarrow [\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} = 6.61\times10^{-5}\ \mathrm{M} = [\mathrm{OCl^-}]$$

$$[\mathrm{HOCl}] = (0.150 - 6.61\times10^{-5})\ \mathrm{M} \approx 0.150\ \mathrm{M}$$

$\therefore$ $\boldsymbol{K_a = 2.9\times10^{-8}}$ $\quad$ $\mathrm{p}K_a = -\log(K_a) = 7.54$

pH of a Weak Base (or Acid) Solution

For NH_3(aq), pK_b = 4.75. Find the pH of a 0.025 M aqueous solution of NH_3.

Solution: $K_b = [OH^-]\,[NH_4^+] / [NH_3] = 10^{-4.75} = 1.8\times10^{-5}$

Let C_b = initial concentration of base = 0.025 M

Reaction	NH_3 +	H_2O $\leftrightharpoons$	OH^- +	NH_4^+	
Initial	C_b	-	0	0	M
Change	$-x$	-	$+x$	$+x$	M
Equil.	C_b-x	-	x	x	M

$K_b = x^2/(C_b-x)$ Must have $0 < x < C_b$.

Now solve for x.

Weak Base Solution - continued

Previous slide: $K_b = x^2/(C_b - x)$, $C_b = 0.025$ M, $K_b = 1.8\times10^{-5}$

Approximation: Since the base is weak, x might be small. Try assuming that $x << C_b$ so that $C_b - x \approx C_b$. Then

$$x^2 \approx K_b\, C_b \qquad \therefore\ x \approx (K_b\, C_b)^{½} = 6.7\times10^{-4}$$

Check: $x/C_b = 0.027$, so assumption is OK.

$[OH^-] = x = 6.7\times10^{-4}$ M $\Rightarrow$ pOH = 3.17 **pH = 10.83**

Using the quadratic equation gives $x = 6.6\times10^{-4}$, pH = 10.82.

Because concentrations are approximations to activities, the accuracy is worse than this.

Degree of Ionization

The extent to which an acid (or base) ionizes depends on the pH and the pK_a (or pK_b).

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad K_a = [H_3O^+][A^-]/[HA]$$

Rearrange: $[A^-] / [HA] = K_a / [H_3O^+] = 10^{(pH - pKa)}$

- If pH = pK_a, $[A^-] = [HA]$; half the acid is ionized.
- If pH > pK_a, $[A^-] > [HA]$; more than half is ionized.
- If pH < pK_a, $[A^-] < [HA]$; less than half is ionized.

At any given pH, the lower the pK_a, the greater the degree of ionization.

Degree of Ionization - Significance

If you can recognize whether an acid or base is mostly ionized or slightly ionized, you can tell what approximation to make.

Consider a 0.025 M aqueous solution of NH_3 ($pK_b = 4.75$).

What will be the pOH if the NH_3 fully ionizes? 1.6

Will the degree of ionization be high or low? low

Consider a 1.0×10^{-6} M aqueous solution of NH_3.

What will be the pOH if the NH_3 fully ionizes? 6.0

Will the degree of ionization be high or low? High

In very dilute solutions, weak bases and acids fully ionize.

Dilute Solution of a Weak Base (or Acid)

For $NH_3(aq)$, $pK_b = 4.75$. Find the pH of a 1.0×10^{-6} M aqueous solution of NH_3.

Solution: $K_b = 1.8\times10^{-5} >> [NH_3]$; degree of ionization is large.

Let C_b = initial concentration of base = 1.0×10^{-6} M

Reaction	NH_3 +	H_2O	$\rightleftharpoons OH^-$ +	NH_4^+	
Initial	0	-	C_b	C_b	M
Change	x	-	$-x$	$-x$	M
Equil.	x	-	$C_b - x$	$C_b - x$	M

Assume $x << C_b$ $\therefore$ $x \approx C_b^2/K_b = 5.6\times10^{-8}$. Approx. is OK.

$pOH = -\log(1.0\times10^{-6}) = 6.00$ **pH = 8.00**.

Very Dilute Solutions

Q: What is the pH of a 1.0×10^{-6} M solution of HNO_3?

A: $pH = -\log[1.0\times10^{-6}] = 6.00$

Q: What is the pH of a 1.0×10^{-7} M solution of HNO_3?

A: $pH = -\log[1.0\times10^{-7}] = 7.00$? ***Neutral?*** Very suspicious.

Q: What is the pH of a 1.0×10^{-8} M solution of HNO_3?

A: $pH = -\log[1.0\times10^{-8}] = 8.00$?***Obviously wrong!***

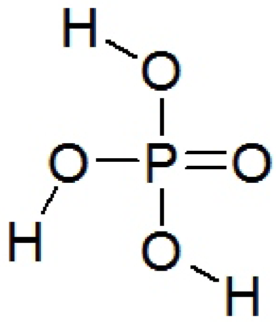
Something is missing. Adding acid can't make water basic.

For 1.0×10^{-8} M HNO_3 in water, there are ***two*** acids: HNO_3 and H_2O.

Polyprotic Acids have Multiple pK_a's

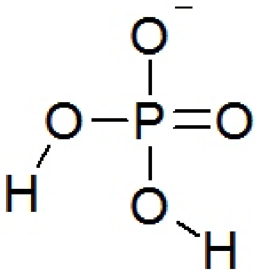
Polyprotic acids are compounds have more than one acidic hydrogen atom. Often, all the protons are equivalent.

Once one proton is gone, the others are in a changed environment and have a higher pK_a.



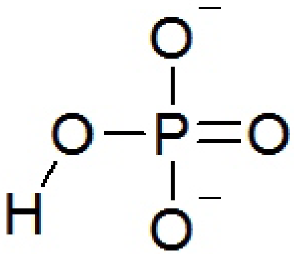
H_3PO_4

pK_a= 2.12



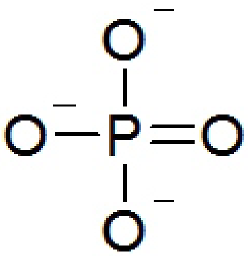
$H_2PO_4^-$

pK_a= 7.21



HPO_4^{2-}

pK_a= 12.76



PO_4^{3-}

Note that $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic.

pH of a Polyprotic Acid Solution

Calculations are best done in a stepwise manner:

- Treat the first ionization as if it were the only one. Calculate the pH and the degree of ionization.
- Use the pH from step (1) to calculate the degree of the second ionization. If it is small, it does not affect the pH; so we are done. (See example 16-9 in the text.)
- If the first ionization is complete, the second can be solved using an ICE table. (Example 16-10 in the text.)
- If the second ionization is complete, move on to the third one. And so on.

If two ionizations are incomplete, more complex calculations are needed.

Acid-Base Calculations - Summary

- A solution may have several acid-base reactions. You must decide which reaction is the important one.
- Before starting the calculation, think about the appropriate starting point.
- The equilibrium condition must be satisfied.
- Material balance must be satisfied. The ICE table is an easy way to account for this.
- Simplifying assumptions are helpful in getting an answer.
- Always check the validity of the simplifying assumption. If not valid, the starting point may need to be changed.

Hydrolysis of Salts - Section 16.7

Salts dissolve in water to produce ions. The ions might undergo proton transfer with water.

The conjugate base of a weak acid is a weakly basic anion.
The conjugate acid of a weak base is a weakly acidic cation.

In aqueous solution, salts can act as acids and/or bases. These are called **hydrolysis** reactions.

Example:

dissolution: $NH_4NO_3(s) \rightleftharpoons NH_4^+(aq) + NO_3^-(aq)$

hydrolysis: $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

NH_4NO_3 acts as an acid in solution

Hydrolysis of Salts - continued

Example:

dissolution: $NaF(s) \rightleftharpoons Na^+(aq) + F^-(aq)$

hydrolysis: $F^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HF(aq)$

NaF acts as a base in solution

The Na^+ ion in solution is

a) acidic

b) basic

c) pH neutral

pH of Salt Solutions

Hydrolysis reactions change the pH.

Whether a salt acts as an acid or a base depends on the strengths of the acid and base that form the salt.

Salt of a strong acid and a strong base

Example: $MgBr_2$ is a salt of HBr and $Mg(OH)_2$.

dissolution: $MgBr_2(s) \leftrightharpoons Mg^{2+}(aq) + 2Br^{-}(aq)$

hydrolysis: $Mg^{2+} + 2H_2O \leftrightharpoons 2H_3O^{+} + Mg(OH)_2$ insignificant

hydrolysis: $Br^{-} + H_2O \leftrightharpoons OH^{-} + HBr$ insignificant

No significant hydrolysis. **pH = 7**

pH of Salt Solutions - continued

Salt of a strong acid and a weak base

NH_4NO_3 is a salt of HNO_3 and NH_3 (pK_b=4.74).

dissolution: $NH_4NO_3(s) \leftrightharpoons NH_4^+(aq) + NO_3^-(aq)$

hydrolysis: $NH_4^+ + H_2O \leftrightharpoons H_3O^+ + NH_3$ favorable

hydrolysis: $NO_3^- + H_2O \leftrightharpoons OH^- + HNO_3$ insignificant

Conjugate acid of the weak base hydrolyzes.

$pH < 7$

pH of Salt Solutions - continued

Salt of a weak acid and a strong base

NaF is a salt of HF (pK_a=3.18) and NaOH.

dissolution: $NaF(s) \rightleftharpoons Na^{+}(aq) + F^{-}(aq)$

hydrolysis: $Na^{+} + H_2O \rightleftharpoons H_3O^{+} + NaOH$ insignificant

hydrolysis: $F^{-} + H_2O \rightleftharpoons OH^{-} + HF$ favorable

Conjugate base of the weak acid hydrolyzes.

$pH > 7$

pH of Salt Solutions - continued

Salt of a weak acid and a weak base

NH_4F is a salt of HF (pK_a=3.18) and NH_3 (pK_b=4.74).

dissolution: $NH_4F(s) \rightleftharpoons NH_4^+(aq) + F^-(aq)$

hydrolysis: $NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$ favorable

hydrolysis: $F^- + H_2O \rightleftharpoons OH^- + HF$ favorable

Both ions hydrolyze. Is the solution acidic or basic?

For NH_4^+, pK_a = 14.00 − 4.74 = 9.26

For F^-, pK_b = 14.00 − 3.18 = 10.82

Since pK_a < pK_b, hydrolysis of NH_4^+ is more favorable, therefore **pH < 7**. (Same result if comparing HF and NH_3.)

Hydrolysis of Salts - Summary

For a salt:

- The cation may be the conjugate acid of a base.
- The anion is the conjugate base of an acid.
- Anions and cations may undergo hydrolysis.
- The pH of the solution depends on which hydrolysis reaction is more favorable.
- The hydrolysis reaction with the lower p*K* (higher *K*) is the more favorable one.