Chapter 15: Acids and Bases

Common Household Acids & Bases
Acids   Bases

Acids and Bases

Arrhenius Definitions:
- *acids* - compounds that produce an increase in $[H^+]$ when dissolved in water
- *bases* - compounds that produce an increase in $[OH^-]$ when dissolved in water

Lewis Definitions:
- *acids* - electron pair acceptors
- *bases* - electron pair donors

Brønsted-Lowry Definitions:
- *acids* - H^+ donors
- *bases* - H^+ acceptors
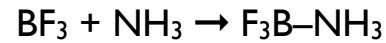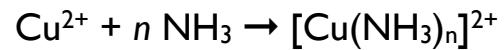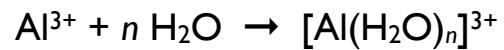
Lewis Acids & Lewis Bases

- more broad way to define acids and bases

- Lewis acids – electron pair acceptors
  metal cations (M^{n+}) and boron are common Lewis acids

  species that are *electron deficient*; *electrophiles*

- Lewis bases – electron pair donors
  species with O, N, halogen frequently have lone pairs of electrons to share ∴ Lewis bases

  species that are *electron rich*; *nucleophiles*

- product of a Lewis Acid + Lewis Base reaction is called a *Lewis Acid-Base adduct*

Lewis Acids & Lewis Bases

- some examples:

$$Al^{3+} + n\ H_2O \rightarrow [Al(H_2O)_n]^{3+}$$

$$Cu^{2+} + n\ NH_3 \rightarrow [Cu(NH_3)_n]^{2+}$$

$$BF_3 + NH_3 \rightarrow F_3B–NH_3$$
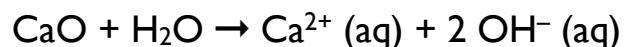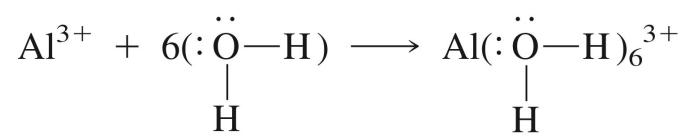
- acidic oxides (oxides of nonmetals):

$$SO_3 + H_2O \rightarrow H_2SO_4$$
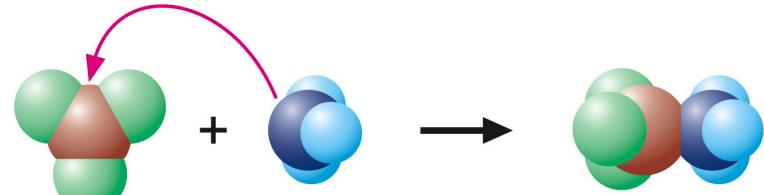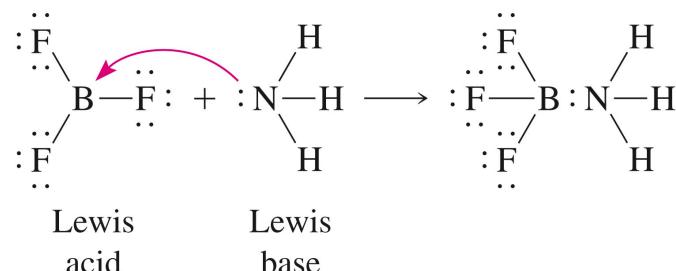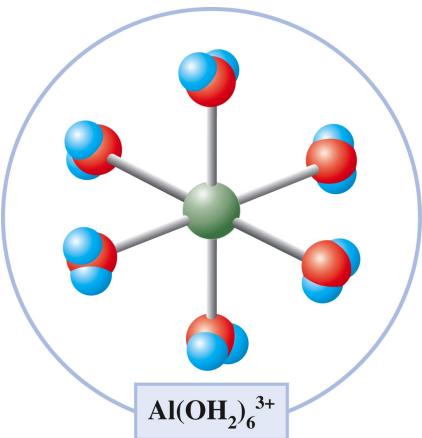
- basic oxides (oxides of metals):

$$CaO + H_2O \rightarrow Ca^{2+}\ (aq) + 2\ OH^-\ (aq)$$

Top-left panel

$$Al^{3+} + 6(\overset{..}{:}\overset{..}{O}—H) \longrightarrow Al(\overset{..}{:}\overset{..}{O}—H)_6^{3+}$$

(with H below each O)

Lewis acid   Lewis base

$Al(OH_2)_6^{3+}$

Top-right panel

$$\overset{..}{:}\overset{..}{F}—B—\overset{..}{:}\overset{..}{F} \; + \; :N—H \longrightarrow \overset{..}{:}\overset{..}{F}—B:N—H$$

(B bonded to two F; N bonded to H atoms)
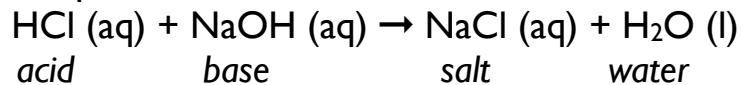
Lewis acid   Lewis base

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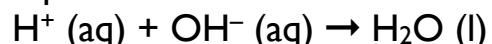
Brønsted-Lowry Acids & Bases

- Brønsted-Lowry acids – H^+ donors

- Brønsted-Lowry bases – H^+ acceptors

- reaction of a Brøsted-Lowry acid + base is a *neutralization* reaction
  characterized by H^+ transfer

example of neutralization reaction:
   HCl (aq) + NaOH (aq) → NaCl (aq) + H_2O (l)
   acid   *base*   *salt*   *water*

net ionic equation:
      H^+ (aq) + OH^- (aq) → H_2O (l)

Bottom-right panel
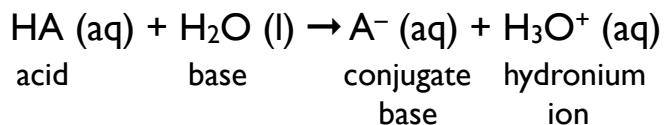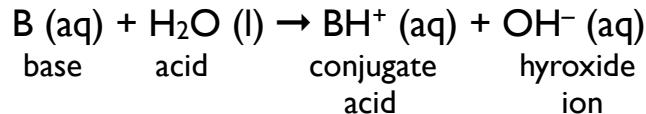
Brønsted-Lowry Acids & Bases
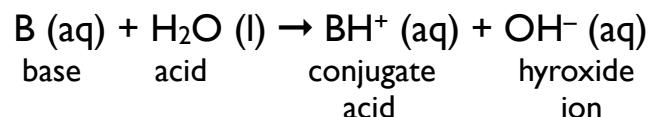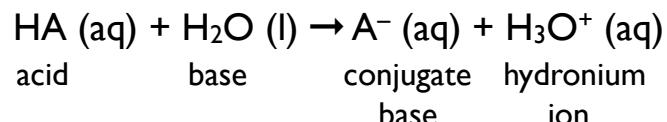
- writing ionization (or *dissociation*) equations to describe Brønsted-Lowry acid/base behavior in aqueous solutions:

- acid ionization (or *dissociation*) equation:

   HA (aq) + H_2O (l) → A^- (aq) + H_3O^+ (aq)
   acid   base   conjugate   hydronium
                          base   ion

- base ionization (or *dissociation*) equation:

   B (aq) + H_2O (l) → BH^+ (aq) + OH^- (aq)
   base   acid   conjugate   hyroxide
                          acid   ion

Brønsted-Lowry Acids & Bases

$$HA \ (aq) + H_2O \ (l) \rightarrow A^- \ (aq) + H_3O^+ \ (aq)$$

acid   base   conjugate   hydronium
                        base   ion

$$B \ (aq) + H_2O \ (l) \rightarrow BH^+ \ (aq) + OH^- \ (aq)$$

base   acid   conjugate   hyroxide
                        acid   ion

some terminology:

amphoteric: a species that can act as an acid <u>or</u> a base

           water is an example of an amphoteric species

conjugate base: species that remains after an acid
               donates its H^+

conjugate acid: species that forms after a base accepts a H^+

Brønsted-Lowry Acids & Bases

some specific examples:
acid ionization equation for nitrous acid:
$$HNO_2 \ (aq) + H_2O \ (l) \rightarrow NO_2^- \ (aq) + H_3O^+ \ (aq)$$
    notes: HNO_2 acid H_2O base
   * H_3O^+ conjugate acid *
                NO_2^- conjugate base
                * H_3O^+ & H^+ *are used*
   *interchangeably*
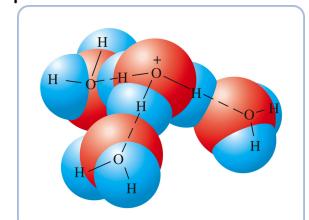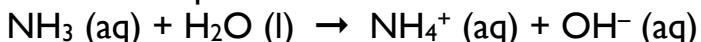
base ionization equation for ammonia:
$$NH_3 \ (aq) + H_2O \ (l) \rightarrow NH_4^+ \ (aq) + OH^- \ (aq)$$
    notes: H_2O acid NH_3 base
           NH_4^+ conjugate acid OH^- conjugate base

Identify each species in the following equation as etiher the Brønsted-Lowry acid, the Brønsted-Lowry base, the conjugate acid, or the conjugate base.

Identify the conjugate acid-base pairs in the reaction.

$$H_2SO_4 \ (aq) + HPO_4^{2-} \ (aq) \rightarrow HSO_4^- \ (aq) + H_2PO_4^- \ (aq)$$

Strong vs. Weak Acids and Bases

Acid and base strength is based on the *extent of ionization* that occurs when the substance is dissolved in water.
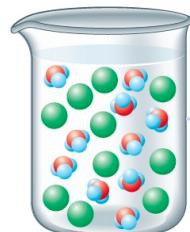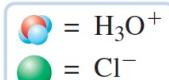
<u>Strong Acids:</u>
- strong electrolytes - completely ionized in solution

- there are 6 strong acids - *KNOW THEM!*
    HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4 (diprotic)
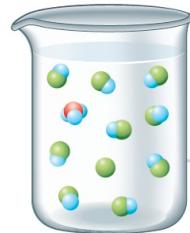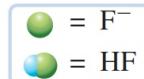
<u>Weak Acids:</u>
- weak electrolytes - partially ionized (typically < 5%) in aqueous solution

- any acid that is not a strong acid is a weak acid
   *some examples*: HF, H_2CO_3, H_3PO_4, HNO_2, $HBrO_4$

Strong vs. Weak Acids and Bases

= H_3O^+
= Cl^-

Due to its complete reaction with water, the strong acid HCl exists as the hydronium ion, $H_3O^+(aq)$, and $Cl^-(aq)$ in aqueous solution. Because of this complete reaction, there are essentially no HCl(aq) molecules in the solution.

= F^-
= HF
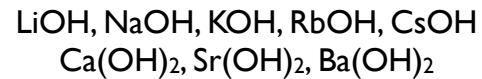
Due to the reaction with only very few water molecules, the weak acid HF(aq) exists in aqueous solution largely as HF(aq) molecules, with very little $H_3O^+(aq)$ and $F^-(aq)$ being produced.

Strong vs. Weak Acids and Bases

Strong Bases:

- strong electrolytes - completely ionized in solution

- the strong bases are the hydroxides of the alkali metals & hydroxides of most alkaline earth metals; *KNOW THEM*!

    LiOH, NaOH, KOH, RbOH, CsOH
    $Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$
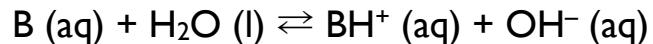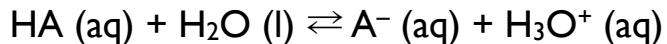
Weak Bases:

- weak electrolytes - partially ionized (typically < 5%) in aqueous solution

- weak bases tend to be organic compounds that contain nitrogen; ammonia and substituted amines
    some examples: NH_3, $(CH_3)NH_2$, $(CH_3)_3N$
 C_5H_5N, N_2H_4, NH_2OH
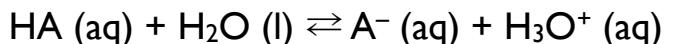
Weak Acids and Weak Bases: Reversible H^+ Transfer Reactions

- In Chapter 4 we defined weak acids and weak bases as weak electrolytes (*only partially ionized in aqueous solution*).

- Now we can talk about their behavior in terms of an equilibrium that exists in solution:

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

    $$B\ (aq) + H_2O\ (l) \rightleftharpoons BH^+\ (aq) + OH^-\ (aq)$$
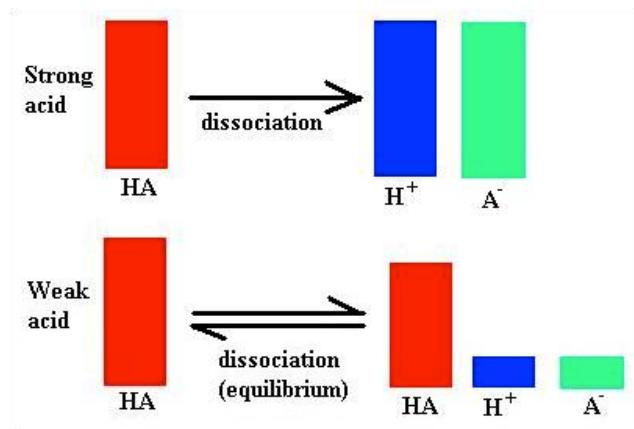
- These are heterogeneous equilibria.

- We will discuss/define equilibrium constants, K_a & K_b.

Weak Acids and Acid Ionization Constant, K_a

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

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

- K_a is the acid ionization constant

- the larger the value of K_a . . .
    the equilibrium position lies farther to the right
    higher $[H_3O^+]$
    greater extent of ionization
    stronger acid

Panel 1 (top-left)

Strong acid — dissociation — HA → H⁺ A⁻

Weak acid — dissociation (equilibrium) — HA ⇌ HA H⁺ A⁻

Panel 2 (top-right)

Weak Bases and Base Ionization Constant, K_b

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

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- K_b is the base ionization constant

- the larger the value of K_b …
  the equilibrium position lies farther to the right
  higher $[OH^-]$
  greater extent of ionization
  stronger base

Panel 3 (bottom-left)

Relationship Between Strengths in Conjugate Acid/Base Pairs

- the *stronger* an acid, the *weaker* its conjugate base

- the *weaker* an acid, the *stronger* its conjugate base

- the *stronger* a base, the *weaker* its conjugate acid

- the *weaker* a base, the *stronger* its conjugate acid

Table 15.2 Relative Strengths of Acids and Bases

	Acid	Base	
Strongest acids	$HClO_4$	ClO_4^-	Weakest bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	H_3O^+	H_2O	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	$HC_2H_3O_2$	$C_2H_3O_2^-$	
	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5OH^{2+}$	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	$HClO$	ClO^-	
	$HBrO$	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
	HS^-	S^{2-}	
Weakest acids	H_2O	OH^-	Strongest bases

Panel 4 (bottom-right)

Table 16.1 Acid-Ionization Constants at 25°C*

Substance	Formula	K_a
Acetic acid	$HC_2H_3O_2$	1.7×10^{-5}
Benzoic acid	$HC_7H_5O_2$	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
	HCO_3^-	4.8×10^{-11}
Cyanic acid	$HOCN$	3.5×10^{-4}
Formic acid	$HCHO_2$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulfate ion	HSO_4^-	1.1×10^{-2}
Hydrogen sulfide	H_2S	8.9×10^{-8}
	HS^-	$1.2 \times 10^{-13\dagger}$

Hypochlorous acid	HClO	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$H_2C_2O_4$	5.6×10^{-2}
	$HC_2O_4^{-}$	5.1×10^{-5}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
	$H_2PO_4^{-}$	6.2×10^{-8}
	HPO_4^{2-}	4.8×10^{-13}
Phosphorous acid	H_2PHO_3	1.6×10^{-2}
	$HPHO_3^{-}$	7×10^{-7}
Propionic acid	$HC_3H_5O_2$	1.3×10^{-5}
Pyruvic acid	$HC_3H_3O_3$	1.4×10^{-4}
Sulfurous acid	H_2SO_3	1.3×10^{-2}
	HSO_3^{-}	6.3×10^{-8}

Table 16.2 Base-Ionization Constants at 25°C

Substance	Formula	K_b
Ammonia	NH_3	1.8×10^{-5}
Aniline	$C_6H_5NH_2$	4.2×10^{-10}
Dimethylamine	$(CH_3)_2NH$	5.1×10^{-4}
Ethylamine	$C_2H_5NH_2$	4.7×10^{-4}
Hydrazine	N_2H_4	1.7×10^{-6}
Hydroxylamine	NH_2OH	1.1×10^{-8}
Methylamine	CH_3NH_2	4.4×10^{-4}
Pyridine	C_5H_5N	1.4×10^{-9}
Urea	NH_2CONH_2	1.5×10^{-14}

Relationship Between Structure and Strengths of Acids

- Brønsted-Lowry acids are H⁺ donors . . . *so* . . . acid strength is dependent on how readily donated the acidic H⁺ is

- the *weaker* the interaction between A–H (in binary acids) or O–H (in oxoacids), the *stronger the acid*

- the *stronger* the interaction between A–H (in binary acids) or O–H (in oxoacids), the *weaker the acid*

Relationship Between Structure and Strengths of Acids: Binary Acids (HA)

- For a set of binary acids in which *A* belongs to the same group of the periodic table, H–*A* bond strength is the determining factor in acid strength.

    the stronger the H–A bond, the weaker the acid

- H–*A* bond strength is related to atomic size:

    bond strength decreases as atomic radius increases

    atomic radius increases moving down the periodic table

Relationship Between Structure and Strengths of Acids: Binary Acids (HA)

- For a set of binary acids in which A is in the <u>same period</u> of the periodic table, H–A bond *polarity* is the determining factor in acid strength.

  the more polar the H–A bond, the stronger the acid

- H–A bond polarity depends on the electronegativity of A:

  > bond polarity increases as the electronegativity of A increases

  > electronegativity increases moving left to right across the periodic table

Relationship Between Structure and Strengths of Acids: Binary Acids (HA)
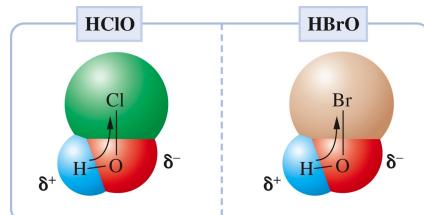
| group/period of A	group VIA	group VIIA
2nd period	H_2O $K_a = 1 \times 10^{-14}$	HF $K_a = 6.8 \times 10^{-4}$
3rd period	H_2S $K_a = 9 \times 10^{-8}$	HCl K_a very large
4th period	H_2Se $K_a = 1.3 \times 10^{-4}$	HBr K_a very large
5th period	H_2Te $K_a = 2.3 \times 10^{-3}$	HI K_a very large

HA bond strength decreases

HA acid strength increases

Electronegativity of A increases
HA bond polarity increases
HA acid strength increases
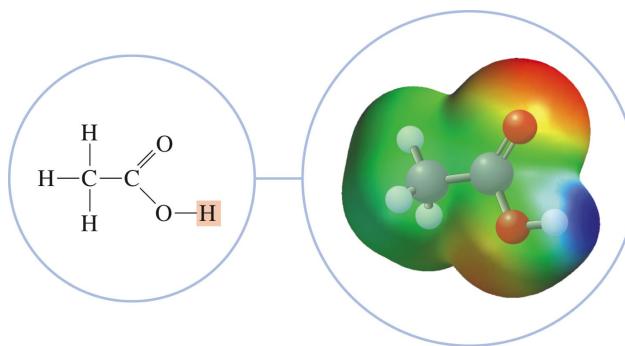
Relationship Between Structure and Strengths of Acids: Oxoacids (H$_n$AO$_m$)

- For a set of oxoacids with the <u>same number of O's</u>, the acid strength increases as the electronegativity of A increases.

- if A is more electronegative, it pulls electron density toward itself resulting in a more polarized O–H bond

  the more polar the O–H bond, the stronger the acid

Carboxylic Acids: O–H Bond Polarization and Acid Strength

- acetic acid (CH_3COOH) has $K_a = 1.8 \times 10^{-5}$

- How will the acid strength change as 1, 2 or 3 H's are replaced with F? With Cl?

Relationship Between Structure and Strengths of Acids: Oxoacids (H_nAO_m)

	acetic acid CH_3COOH $K_a = 1.8 \times 10^{-5}$	
HOI $\chi_I = 2.5$ $K_a = 2.3 \times 10^{-11}$	monofluoroacetic acid CH_2FCOOH $K_a = 2.5 \times 10^{-3}$	monochloroacetic acid $CH_2ClCOOH$ $K_a = 1.4 \times 10^{-3}$
HOBr $\chi_{Br} = 2.8$ $K_a = 2.0 \times 10^{-9}$		dichloroacetic acid $CHCl_2COOH$ $K_a = 5.5 \times 10^{-2}$
HOCl $\chi_{Cl} = 3.0$ $K_a = 3.5 \times 10^{-8}$	trifluoroacetic acid CF_3COOH $K_a = 10$	trichloroacetic acid CCl_3COOH $K_a = 0.23$

Relationship Between Structure and Strengths of Acids: Oxoacids (H_nAO_m)

- For a set of oxoacids with the <u>same atom A</u>, the acid strength increases as the number of O's increases.

- As the number of electronegative O's in the molecule increases, the net effect is that electron density is pulled away from H resulting in a more polarized O–H bond.

   the more polar the O–H bond, the stronger the acid

acid:	HClO	HClO$_2$	HClO$_3$	HClO$_4$
$K_a =$	3.5×10^{-8}	1.2×10^{-2}	~ 1	v. large

Auto-Ionization of Water and K_W

- recall that water is amphoteric - can act as an acid or a base

- now consider a reaction between 2 water molecules:

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

- this is called the auto-ionization of water
   heterogeneous equilibrium
   $$K_W = [H_3O^+][OH^-]$$

   at 25°C, $K_W = 1.0 \times 10^{-14}$

> *In any aqueous solution at 25°C:*
> $$[H_3O^+][OH^-] = K_W = 1.0 \times 10^{-14}$$

Acidic, Basic & Neutral Aqueous Solutions

- distinguish between acidic, basic and neutral solutions based on the relative $[H_3O^+]$ & $[OH^-]$

   if $[H_3O^+] > [OH^-]$, solution is acidic

   if $[OH^-] > [H_3O^+]$, solution is basic

   if $[H_3O^+] = [OH^-]$, solution is neutral

- for a neutral solution at 25°C:

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

example:

In a sample of lemon juice, $[H_3O^+] = 2.5 \times 10^{-3}$ M. Calculate the $[OH^-]$, and classify lemon juice as an acidic, basic or neutral solution.
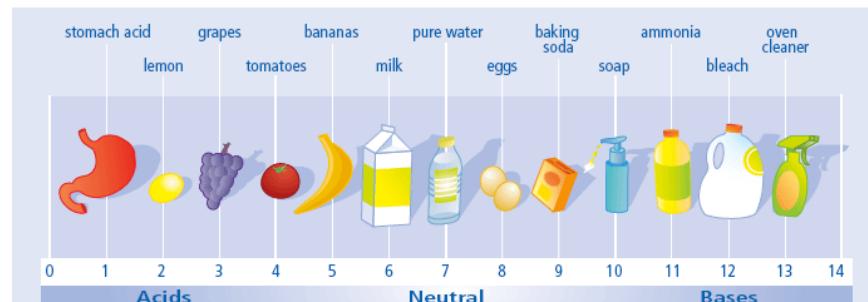

example:

At 50°C, $K_W = 5.5 \times 10^{-14}$. Determine $[H_3O^+]$ and $[OH^-]$ in a neutral solution at 50°C.


The pH Scale
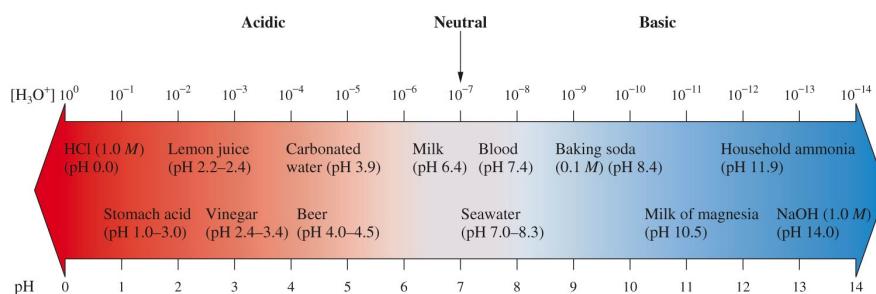
logarithmic scale of $[H_3O^+]$ in solution

$$pH = -\log[H_3O^+]; \quad [H_3O^+] = 10^{-pH}$$

Relationship Between $[H_3O^+]$ and pH

- as $[H_3O^+]$ changes by a factor of 10, the pH of the solution changes by 1 unit

- higher $[H_3O^+]$ corresponds to lower pH

- higher $[H_3O^+]$ corresponds to more acidic solution

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pH Calculations:
Relative Acidity and Basicity of Solutions

recall:

- in any aqueous solution at 25°C:
  $$[H_3O^+][OH^-] = 1 \times 10^{-14}$$

- $pH = -\log[H_3O^+]; \quad [H_3O^+] = 10^{-pH}$

- higher $[H^+]$ ➡ more acidic solution ➡
  lower pH

- higher $[OH^-]$ ➡ lower $[H^+]$ ➡
  more basic solution ➡ higher pH

pH Calculations:
Relative Acidity and Basicity of Solutions

ex: Calculate the pH of 0.00283 M HNO_3 (aq).

ex: Will the pH of 0.00283 M HNO_2 (aq) be less than, greater than, or equal to the pH of 0.00283 M HNO_3 (aq)? Why?

ex: Calculate the $[H_3O^+]$ in a sol'n with pH = 3.61.

ex: Calculate the pH of 0.20 M $Ba(OH)_2$ (aq) and 0.20 M NaOH (aq). Should they be the same? Why or why not?

Other Logarithmic Quantities

• $pOH = - \log [OH^-]$ $[OH^-] = 10^{-pOH}$
  the higher the $[OH^-]$, the lower the pOH
  as $[OH^-]$ changes by factor of 10, the pOH changes by 1 unit

• $pK_a = - \log K_a$ $K_a = 10^{-pK_a}$
  the larger the K_a of an acid, the smaller the pK_a

• $pK_b = - \log K_b$ $K_b = 10^{-pK_b}$
  the larger the K_b of a base, the smaller the pK_b

• $pK_w = - \log K_w$ at 25°C, $pK_w = 14.00$