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ACID-BASE REACTIONS/ THE PH CONCEPT.

Lecture topics.

- 2 lectures dealing with some core chemistry :
  - **acid/base reactions**
  - **the pH concept**.
- We will study these concepts in more detail during the main lecture course later on.
- We will address the following questions/ideas:
  - What are acids and bases?
  - Can we provide a general definition of acid and base?
  - How can we quantify acidity and basicity?
  - Can we classify acid and base strength?
  - pH concept and pH scale.
  - Acid/base reactions: neutralization
  - How can we monitor an acid/base reaction in real time?
    - Acid/base titrations
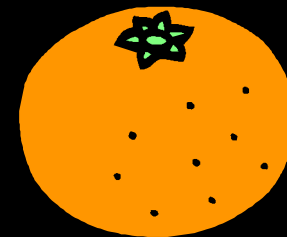
Required Reading Material.

- Silberberg, Chemistry, 4th edition.
  - Chapter 18.
    - Acid/base equilibria. pp.766-813.
  - Chapter 19.
    - Ionic equilibria in aqueous systems. pp.814-862.
- Kotz, Treichel and Weaver, 7th edition.
  - Chapter 17&18, pp.760-859.
- Burrows et al. Chemistry[3] (OUP), 2009.Ch.6, pp.263-300.
- Lecture notes available after course on School of Chemistry website located at:

http://www.tcd.ie/Chemistry/outreach/prelim/

Useful websites

- http://www.shodor.org/unchem/basic/ab/

- http://chemistry.about.com/od/acidsbases/

- http://www.chem.neu.edu/Courses/1221PAM/acidbase/index.htm

- http://dbhs.wvusd.k12.ca.us/webdocs/AcidBase/AcidBase.html

- http://www.sparknotes.com/chemistry/acidsbases/fundamentals/section1.html

Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas
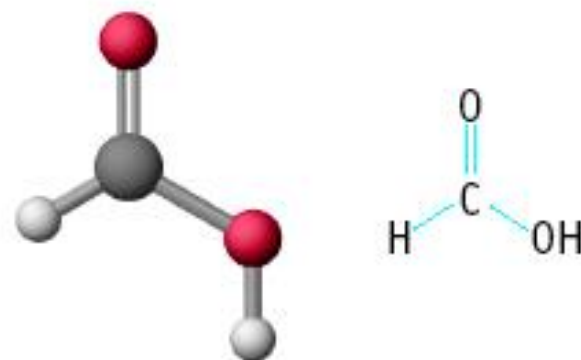
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

4.3

Acid and Bases

The tartness of lemons and oranges comes from the weak acid citric acid. The acid is found widely in nature and in many consumer products. (Charles D. Winters)
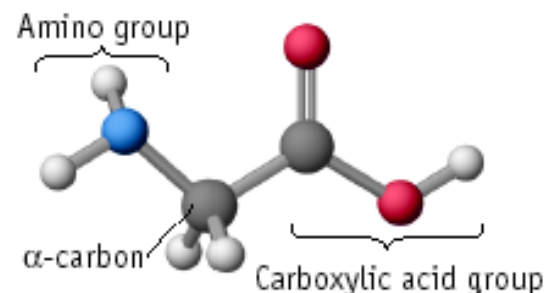
The sting of ants is due to the weak acid formic acid, HCO_2H. (Gallo Images/@ CORBIS)
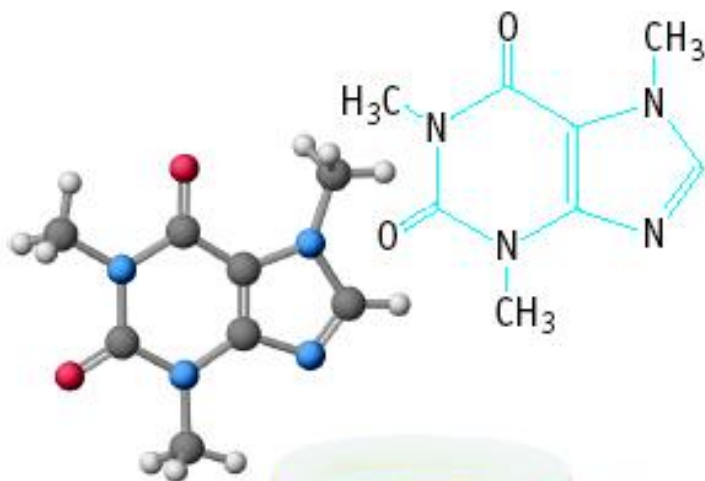
Acid and Bases

HO—C=O

O—C—CH₃ (attached to benzene ring), O

Amino group

α-carbon   Carboxylic acid group
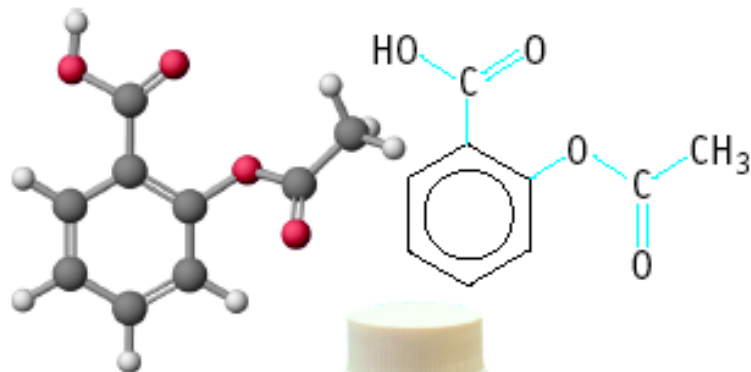
Aspirin is a weak acid that has been used as an analgesic for over 100 years. (Charles D. Winters)

$$H-N-C-C-O-H$$

with H, O above and H, H below

Glycine, $NH_2CH_2CO_2H$
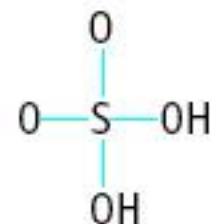
Glycine is representative of the amino acids that are the basis of proteins. The $-CO_2H$ group is the acid portion of the molecule, and the $-NH_2$ group is the basic portion. (Charles D. Winters)

Acid and Bases

Caffeine is a well known stimulant and a weak base. (Charles D. Winters)

A sea slug excretes the strong acid sulfuric acid in self-defense. (Sharksong/ M. Kazmers/Dembinski Photo Associates)
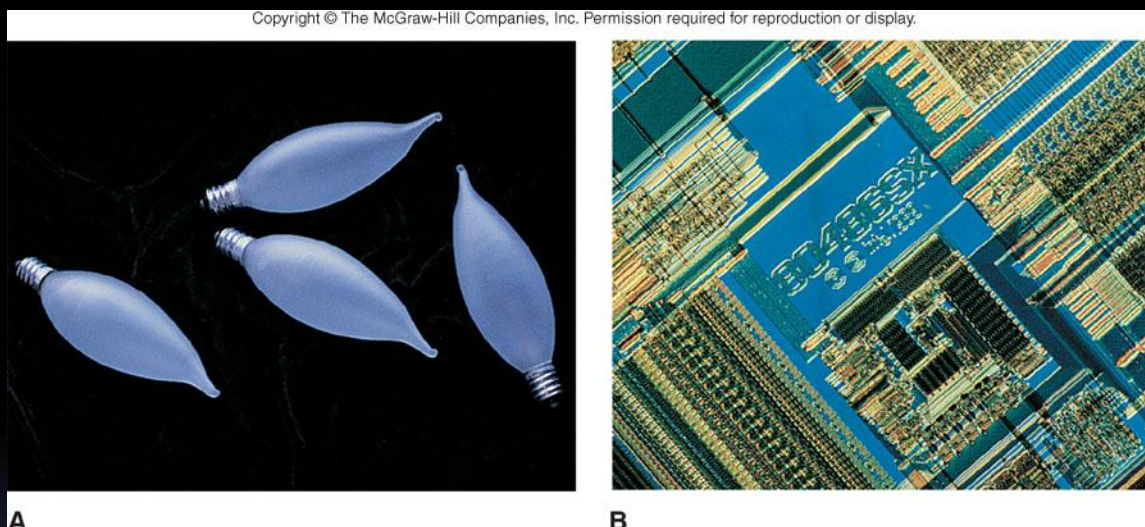
Uses of Common Acids and Bases

18.1 Some Common Acids and Bases and Their Household Uses

| Substance	Formula	Use
Acids		
Acetic acid (vinegar)	CH_3COOH (or $HC_2H_3O_2$)	Flavoring, preservative
Citric acid	$H_3C_6H_5O_7$	Flavoring
Phosphoric acid	H_3PO_4	Rust remover
Boric acid	$B(OH)_3$ (or H_3BO_3)	Mild antiseptic; insecticide
Aluminum salts	$NaAl(SO_4)_2 \cdot 12H_2O$	In baking powder, with sodium hydrogen carbonate
Hydrochloric acid (muriatic acid)	HCl	Brick and ceramic tile cleaner
Bases		
Sodium hydroxide (lye)	$NaOH$	Oven cleaner, unblocking plumbing
Ammonia	NH_3	Household cleaner
Sodium carbonate	Na_2CO_3	Water softener, grease remover
Sodium hydrogen carbonate	$NaHCO_3$	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid
Trisodium phosphate	Na_3PO_4	Cleaner for surfaces before painting or wallpapering

Acid etching

The inside surfaces of these light bulbs are etched with HF.

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A   B

Acids are used to wash away oxides of silicon and metals during the production of computer chips.

Arrhenius (or Classical) Acid-Base Definition

- An *acid* is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions H_3O^+.

- A *base* is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions OH^-.

- *Neutralization* is the reaction of an H^+ (H_3O^+) ion from the acid and the OH^- ion from the base to form water, H_2O.

- These definitions although correct are limited in that they are not very general and do not

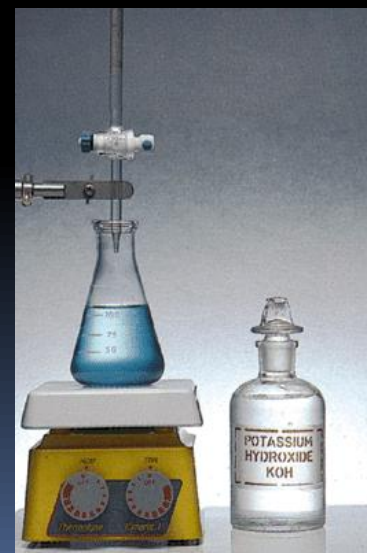- Give a comprehensive idea of what acidity and basicity entails.

$$HCl \rightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH \rightarrow Na^+(aq) + OH^-(aq)$$

$$HCl + NaOH \rightarrow NaCl + H_2O$$
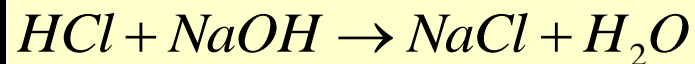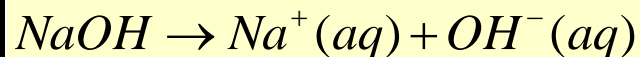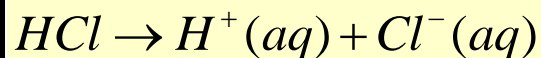
acid   base   salt   water

Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

HCl + H_2O $\longrightarrow$ H_3O^+ + Cl^-
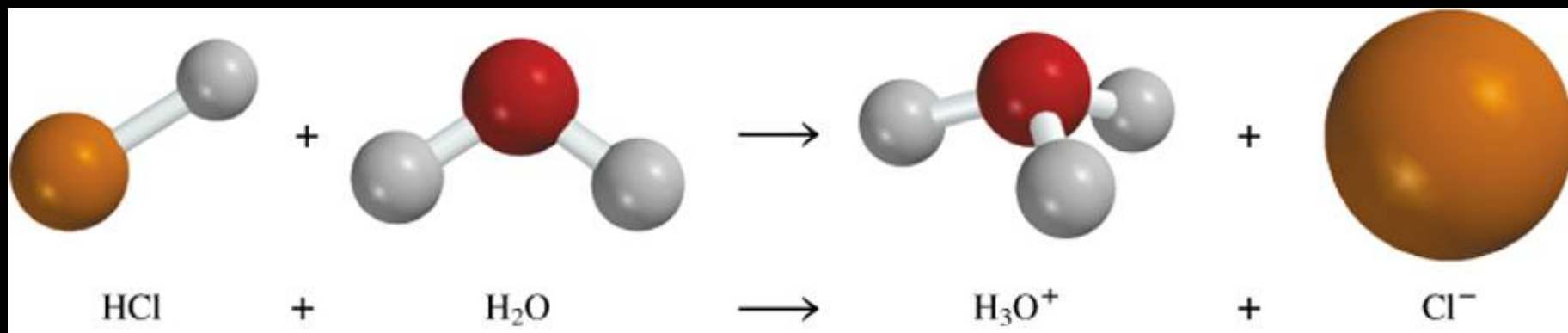
Arrhenius base is a substance that produces OH^- in water

NH_3 + H_2O $\rightleftharpoons$ NH_4^+ + OH^-
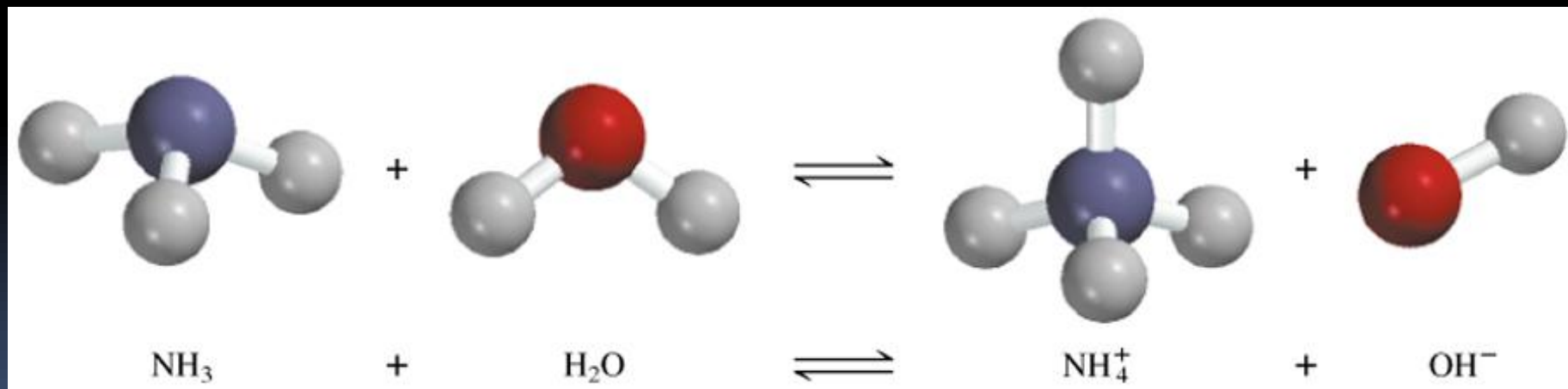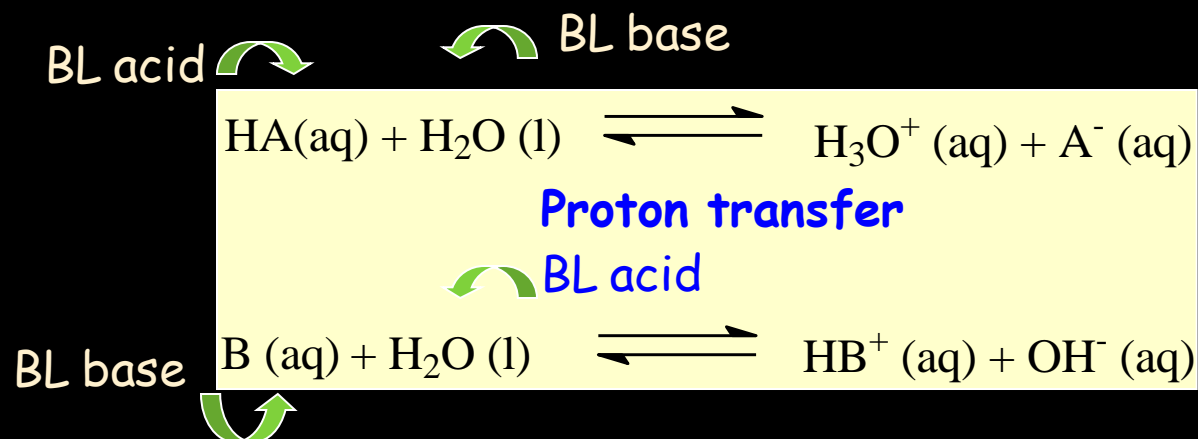
Acids and bases: Bronsted/Lowry definition.

- **Bronsted/Lowry Acid (HA):**
  - An acid is a species which <u>donates</u> a proton
- **Bronsted/Lowry Base (B):**
  - A base is a species which <u>accepts</u> a proton.
- These definitions are quite general and refer to the reaction between an acid and a base.
- An acid must contain H in its formula; HNO_3 and $H_2PO_4^-$ are two examples, all Arrhenius acids are Brønsted-Lowry acids.
- A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3, CO_3^{2-}, F^-, as well as OH^-. Brønsted-Lowry bases are not Arrhenius bases, but all Arrhenius bases contain the Brønsted-Lowry base OH^-.
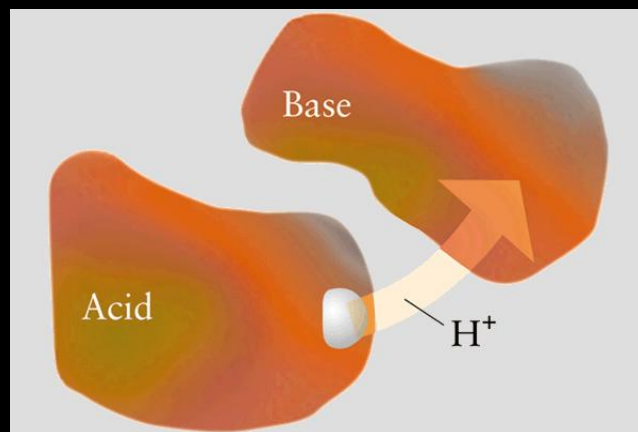
- In the Brønsted-Lowry perspective: one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.

BL acid/base equilibria.

BL acid   BL base

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

Proton transfer

BL acid

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

BL base

Water can function both as an acid and a base depending on the circumstances.

- Proton donation and acceptance are dynamic processes for all acids and bases. Hence a proton transfer equilibrium is rapidly established in solution.
- The equilibrium reaction is described in terms of conjugate acid/base pairs.
- The conjugate base (CB) of a BL acid is the base which forms when the acid has donated a proton.
- The conjugate acid (CA) of a BL base is the acid which forms when the base has accepted a proton.
- A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.
- If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.

Acid : proton donor
Base : proton acceptor

Proton transfer

$$HA \,(aq) + B \,(aq) \rightleftharpoons BH^+ \,(aq) + A^- \,(aq)$$

A   B   CA   CB
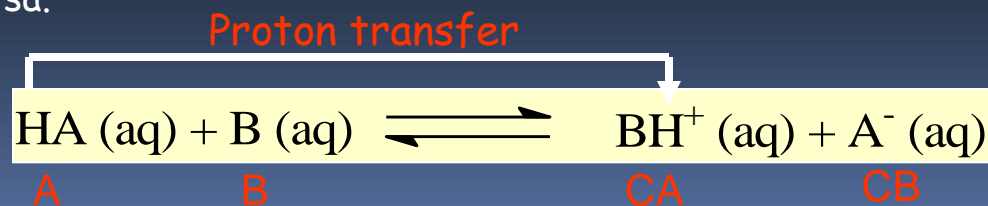
A Brønsted acid is a proton donor
A Brønsted base is a proton acceptor
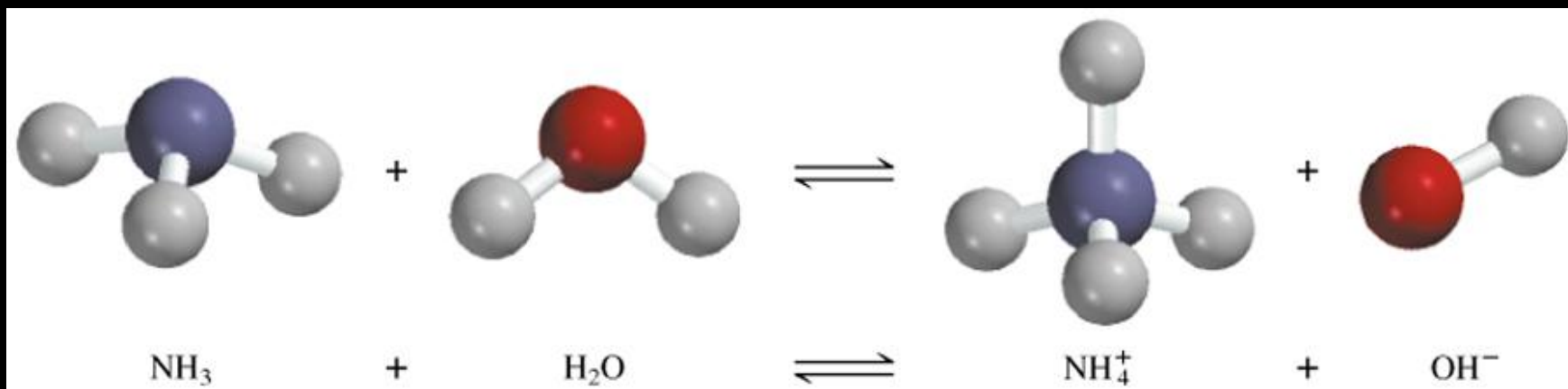
base	acid	acid	base
base	acid	conjugate acid	conjugate base

NH_3 + H_2O ⇌ NH_4^+ + OH^-

The Conjugate Pairs in Some Acid-Base Reactions

Conjugate Pair
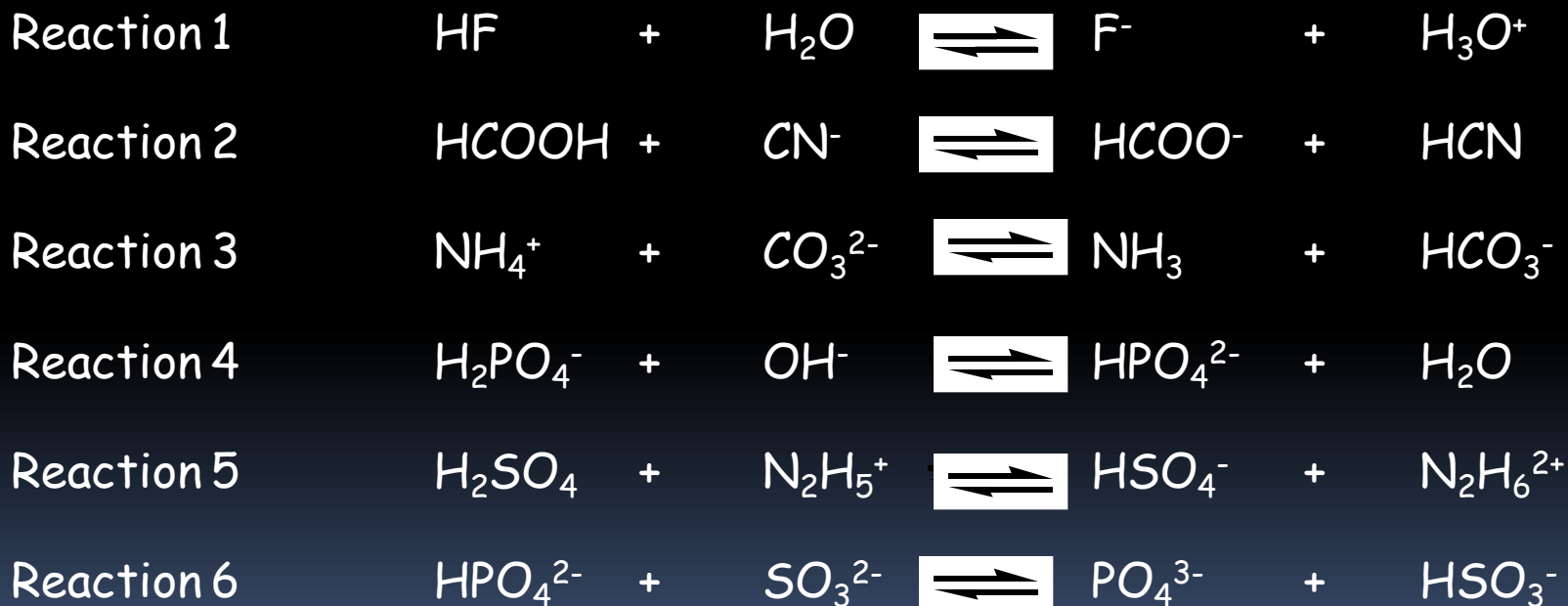
	Acid	+	Base		Base	+	Acid

Conjugate Pair

|							
Reaction 1	HF	+	H_2O	$\rightleftharpoons$	F^-	+	H_3O^+
Reaction 2	$HCOOH$	+	CN^-	$\rightleftharpoons$	$HCOO^-$	+	HCN
Reaction 3	NH_4^+	+	CO_3^{2-}	$\rightleftharpoons$	NH_3	+	HCO_3^-
Reaction 4	$H_2PO_4^-$	+	OH^-	$\rightleftharpoons$	HPO_4^{2-}	+	H_2O
Reaction 5	H_2SO_4	+	$N_2H_5^+$	$\rightleftharpoons$	HSO_4^-	+	$N_2H_6^{2+}$
Reaction 6	HPO_4^{2-}	+	SO_3^{2-}	$\rightleftharpoons$	PO_4^{3-}	+	HSO_3^-

Quantifying acid/base strength.

- How can acid and base strength be quantified?
  - 'Strong' acids vs 'weak' acids
  - 'Strong' bases vs 'weak' bases
  - Key concept is extent or **degree of ionization/dissociation**.
  - Correlation exists between **acid/base strength**, **degree of ionization in solution** and extent to which solution exhibits **ionic conductivity**.

Strong and weak acids.

Battery acid H_2SO_4
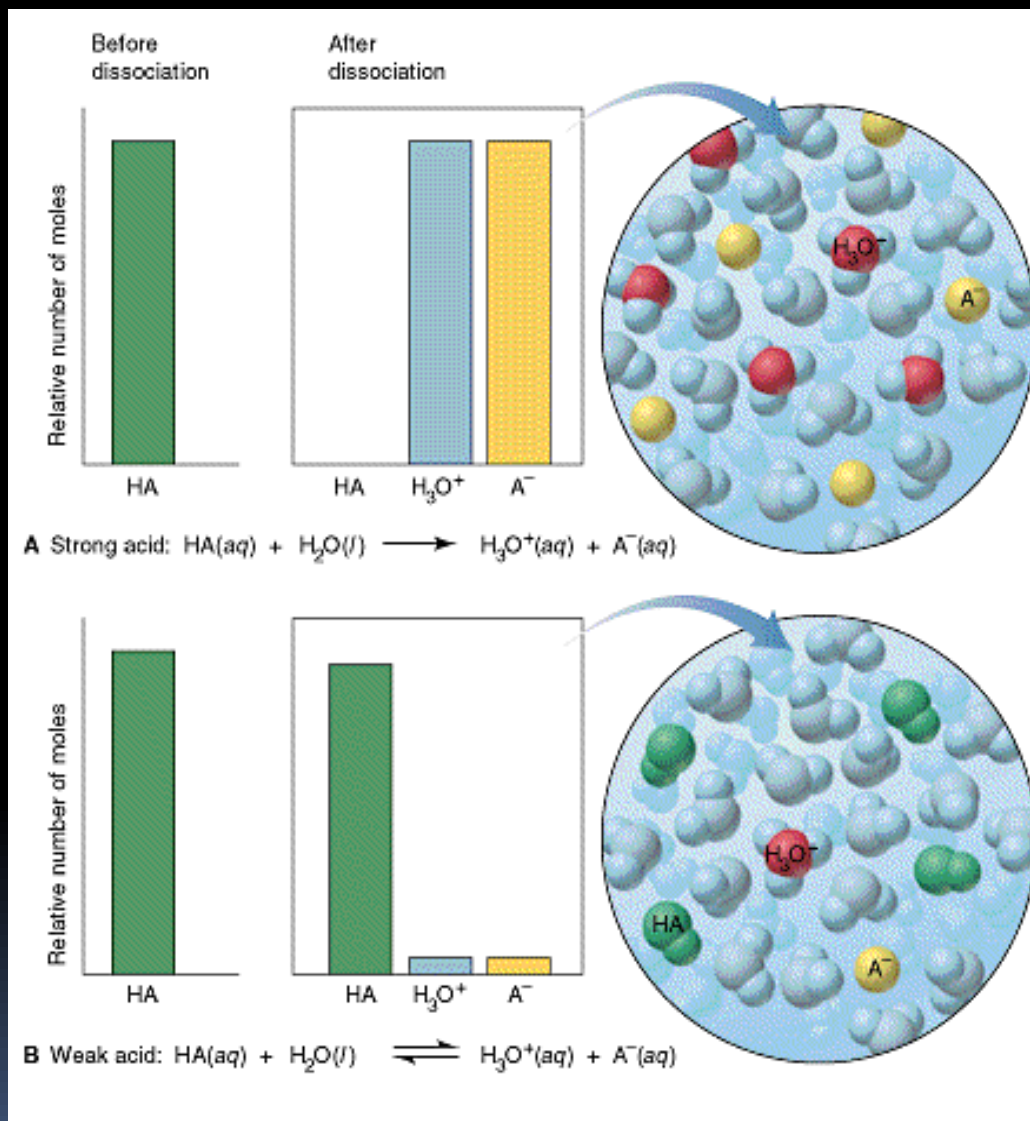

Sulfuric acid

Vinegar

Acetic acid

CH_3COOH
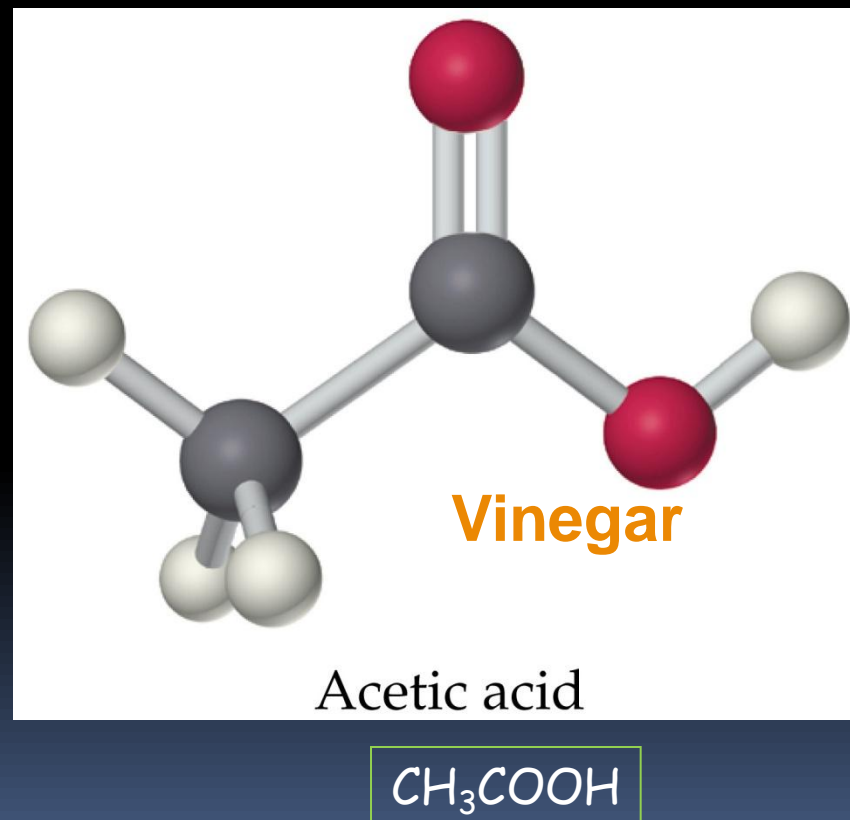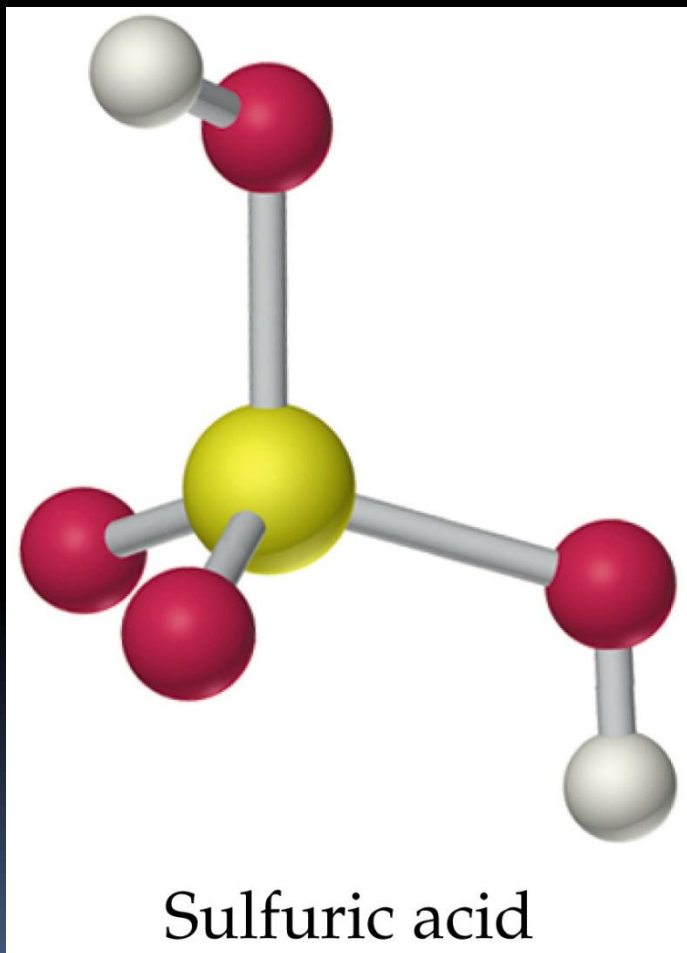
The Extent of Dissociation for Strong and Weak Acids

Key concept :
Acid/base strength quantified in terms of extent or degree of dissociation.
An acid or base is classified as strong if it is fully ionized in solution (e.g. HCl, NaOH).
An acid or base is classified as weak if only a small fraction is ionized in solution (e.g. CH_3COOH, NH_3).

Before dissociation

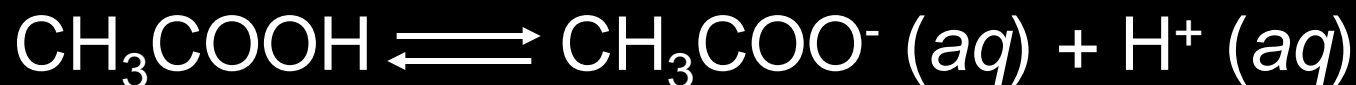After dissociation

Relative number of moles

HA

HA   H$_3$O$^+$ A$^-$

A Strong acid: $HA(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + A^-(aq)$

Relative number of moles

HA

HA   H$_3$O$^+$ A$^-$

B Weak acid: $HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

Partial ionization

Strong Electrolyte – 100% dissociation

$$NaCl\ (s) \xrightarrow{\ H_2O\ } Na^+\ (aq) + Cl^-\ (aq)$$

Weak Electrolyte – not completely dissociated

$$CH_3COOH \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

**Strong Acids** are strong electrolytes

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

$$HNO_3\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

$$HClO_4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + ClO_4^-\ (aq)$$

$$H_2SO4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + HSO_4^-\ (aq)$$

Reactivity of strong and weak acids.

1M HCl(aq)

Strong acid:
Extensive H_2
evolution

1M CH$_3$COOH(aq)

Weak acid:
H_2 evolution
Not very extensive

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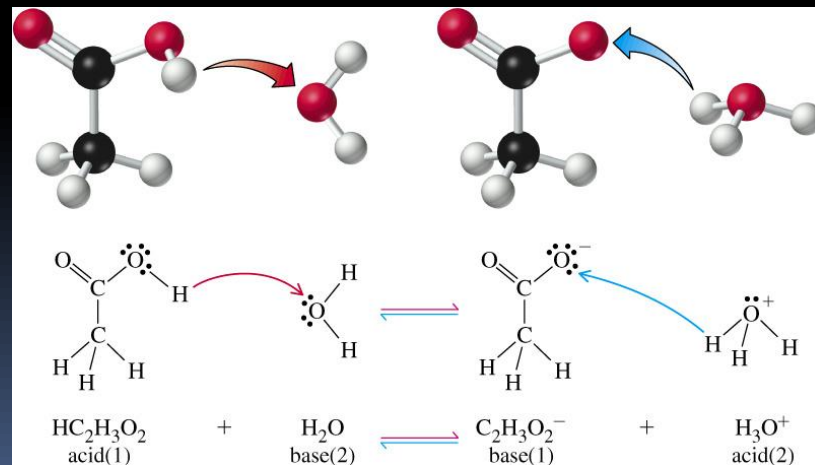
Weak acids/bases.

- We can quantify the extent of dissociation of a weak acid or a weak base in aqueous solution by introducing:
  - the acid dissociation constant K_a

  or
  - the base dissociation constant K_b.

- These are numbers which reflect acid or base strength and are computed by determining the equilibrium concentrations of all relevant species in the solution, and inputting this data into a theoretical expression for the relevant dissociation constant.
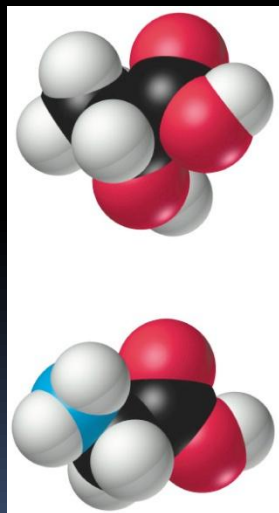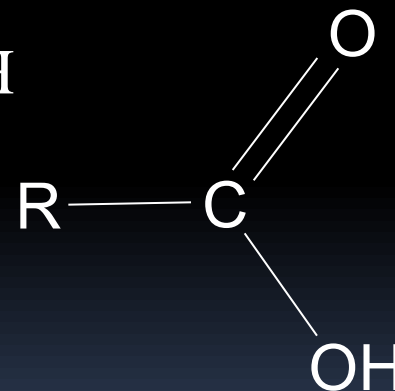
Weak acids.

CH_3CO_2H

Acetic acid

HCl CH_3CO_2H

$$HC_2H_3O_2 \quad + \quad H_2O \quad \rightleftharpoons \quad C_2H_3O_2^- \quad + \quad H_3O^+$$
acid(1)   base(2)   base(1)   acid(2)
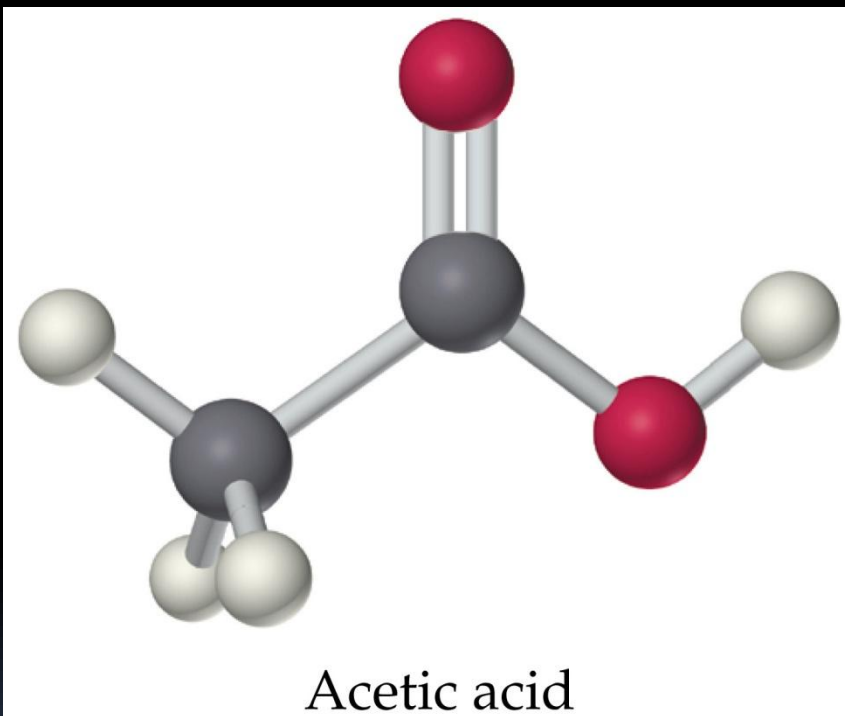
Weak Acids

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

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

lactic acid $CH_3CH(OH)CO_2H$

glycine $H_2NCH_2CO_2H$

Weak Acids are weak electrolytes

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

$$HNO_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NO_2^-\ (aq)$$

$$HSO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + SO_4^{2-}\ (aq)$$

$$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$$
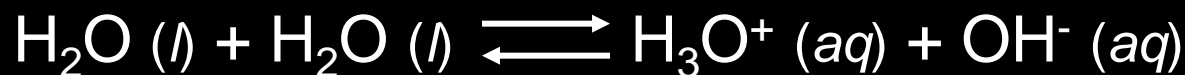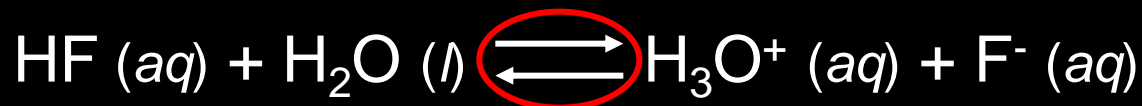
Strong Bases are strong electrolytes

$$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$$

$$KOH\ (s) \xrightarrow{H_2O} K^+\ (aq) + OH^-\ (aq)$$

$$Ba(OH)_2\ (s) \xrightarrow{H_2O} Ba^{2+}\ (aq) + 2OH^-\ (aq)$$

Weak Bases are weak electrolytes

$$F^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HF (aq)$$
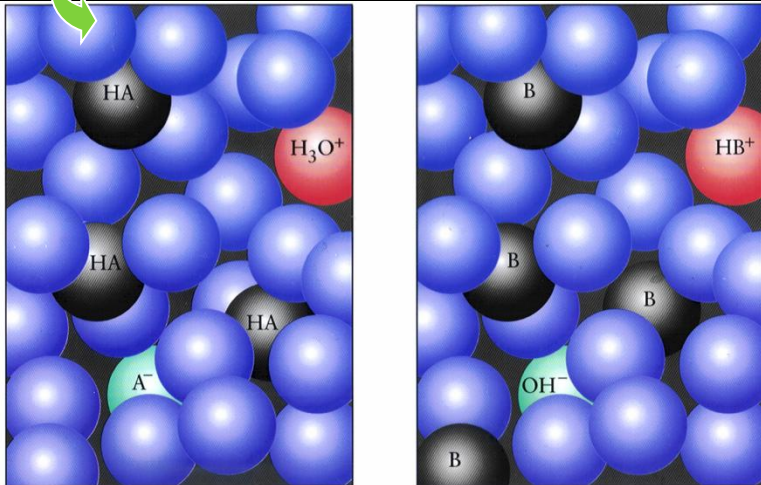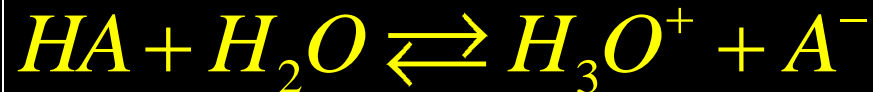
$$NO_2^- (aq) + H_2O (l) \rightleftharpoons OH^- (aq) + HNO_2 (aq)$$
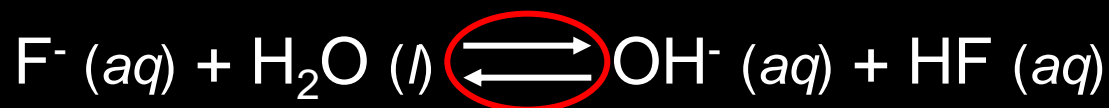
Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.

- H_3O^+ is the strongest acid that can exist in aqueous solution.

- The OH^- ion is the strongest base that can exist in aqeous solution.

Acid/base equilibria.

Weak acid solution at equilibrium

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

HA

H$_3$O$^+$

HA

HA

A$^-$

B

HB$^+$

B

B

B

OH$^-$

B

Figures 3 and 4.14, page 520
Atkins/Jones: *Chemistry: Molecules, Matter, and Change*, **3e**
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Weak base solution at equilibrium

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Mathematical interlude : the logarithm

- Paul Monk, Maths for Chemistry, Oxford University Press, 2006.
- http://en.wikipedia.org/wiki/Logarithm

- The **logarithm** is the mathematical operation that is the inverse of exponentiation (raising a constant, the *base*, to a power). The logarithm of a number x in base b is the number n such that $x = b^n$. It is usually written as $\log_b(x) = n$.

- If $10^x = y$ then $\log_{10} y = x$, e.g. $10^2 = 10 \times 10 = 100$, then $\log_{10}(100) = 2$.

- The **antilogarithm** function is another name for the inverse of the logarithmic function. It is written $\text{antilog}_b(n)$ and means the same as b^n.

- Logarithms can reduce multiplication operations to addition, division to subtraction, exponentiation to multiplication, and roots to division. Therefore, logarithms are useful for making lengthy numerical operations easier to perform .

Mathematical interlude : the logarithm

- The most widely used bases for logarithms are 10, the mathematical constant $e \approx 2.71828...$ and 2. When "log" is written without a base (b missing from log b), the intent can usually be determined from context:
  - natural logarithm (log$e$) in mathematical analysis
  - common logarithm (log10) in engineering and when logarithm tables are used to simplify hand calculations
  - binary logarithm (log2) in information theory and musical intervals .
- The notation "ln(x)" invariably means $\log_e(x)$, i.e., the natural logarithm of x, but the implied base for "log (x)" varies by discipline:
  - Mathematicians generally understand both "ln(x)" and "log(x)" to mean $\log_e(x)$ and write "$\log_{10}(x)$" when the base-10 logarithm of x is intended.
  - Engineers, biologists, and some others write only "ln(x)" or "$\log_e(x)$" when they mean the natural logarithm of x, and take "log (x)" to mean log10(x) or, sometimes in the context of computing, $\log_2(x)$.
  - On most calculators, the LOG button is $\log_{10}(x)$ and LN is $\log_e(x)$.

http://mathworld.wolfram.com/Logarithm.html
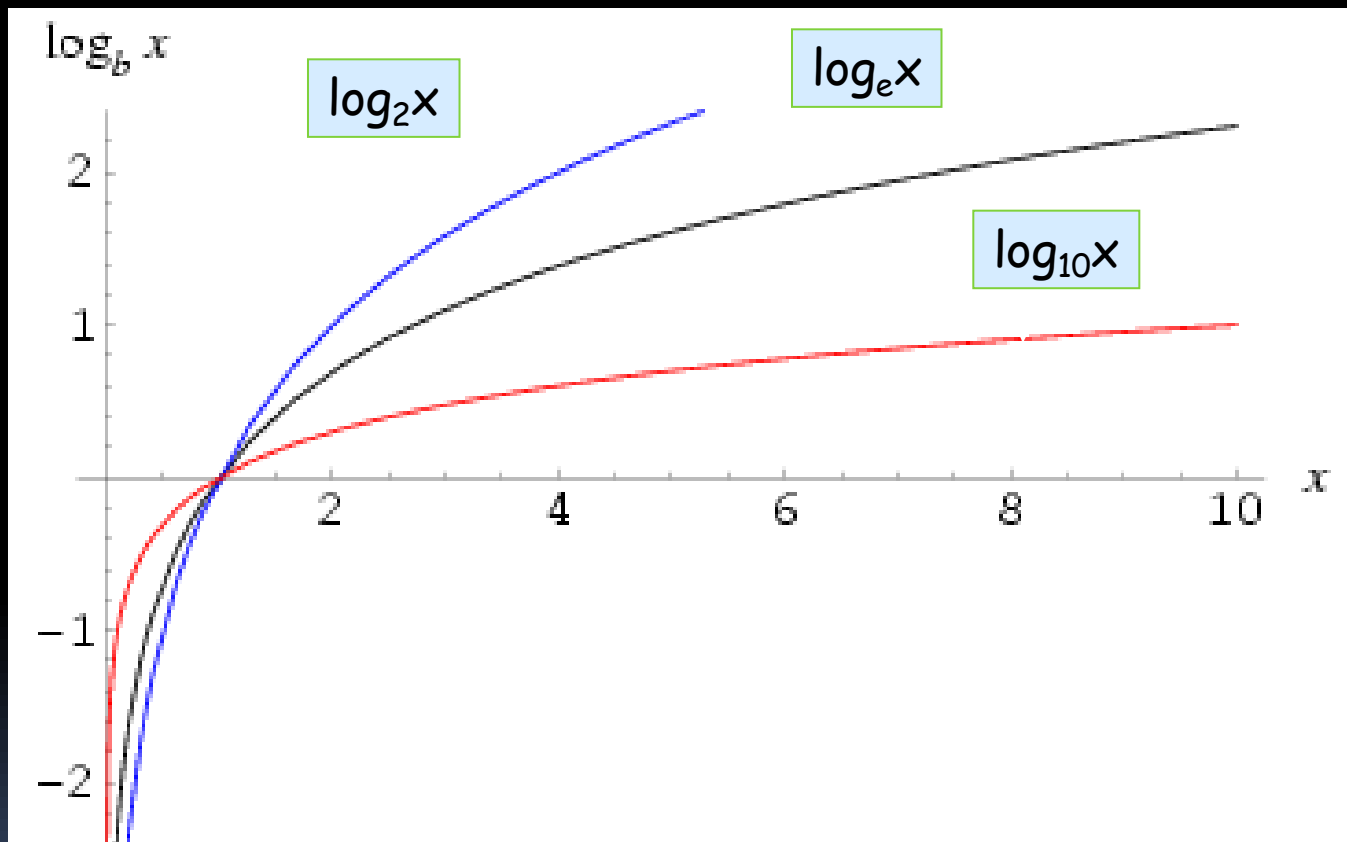
| Operations with numbers	Logarithmic identity
$a.b$	$\log(a.b) = \log(a) + \log(b)$
a/b	$\log(a/b) = \log(a) - \log(b)$
a^b	$\log(a^b) = b\log(a)$
$\sqrt[b]{a}$	$\log(\sqrt[b]{a}) = \log(a)/b$

Acid strength : the acid dissociation constant K_A.

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.

- The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.

- The question is how small is small?

- We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant K_A.

K_A values vary over a wide range so it is best to use a log scale.

$$pK_A = -\log_{10} K_A$$

Acid dissociation equilibrium

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+ (aq) + A^- (aq)$$
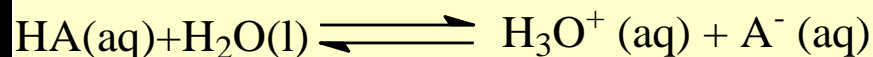
$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_A = K_C[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$
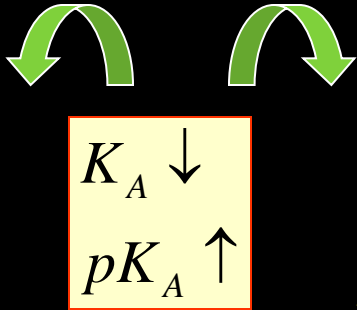
Acid dissociation constant

K_A is a measure of the acid strength. When K_A is large there is considerable Dissociation and the acid is strong. When K_A is small there is a small degree of dissociation, and the acid is weak.

The Relationship Between K_a and pK_a

$$pK_A = -\log_{10} K_A$$

Acid Name (Formula)	K_A at 298 K	pK_A
Hydrogen sulfate ion (HSO_4^-)	1.02×10^{-2}	1.991
Nitrous acid (HNO_2)	7.1×10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol (C_6H_5OH)	1.0×10^{-10}	10.00

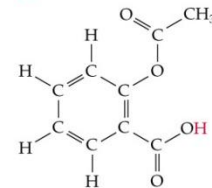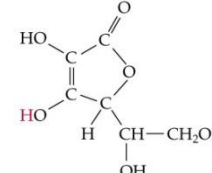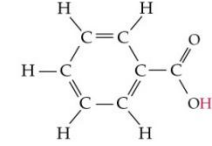$K_A \downarrow$

$pK_A \uparrow$

When K_A is small pK_A is large and the acid does not dissociate in solution to a large extent. A change in 1 pK_A unit implies a 10 fold change in K_A value and hence acid strength.

Ionization Constants of Weak Acids and Bases

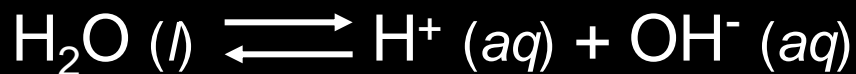|	Ionization Equilibrium	Ionization Constant K	pK
Acid		$K_a =$	p$K_a =$
Iodic acid	$HIO_3 + H_2O \rightleftharpoons H_3O^+ + IO_3^-$	1.6×10^{-1}	0.80
Chlorous acid	$HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$	1.1×10^{-2}	1.96
Chloroacetic acid	$HC_2H_2ClO_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_2ClO_2^-$	1.4×10^{-3}	2.85
Nitrous acid	$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$	7.2×10^{-4}	3.14
Hydrofluoric acid	$HF + H_2O \rightleftharpoons H_3O^+ + F^-$	6.6×10^{-4}	3.18
Formic acid	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$	1.8×10^{-4}	3.74
Benzoic acid	$HC_7H_5O_2 + H_2O \rightleftharpoons H_3O^+ + C_7H_5O_2^-$	6.3×10^{-5}	4.20
Hydrazoic acid	$HN_3 + H_2O \rightleftharpoons H_3O^+ + N_3^-$	1.9×10^{-5}	4.72
Acetic acid	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$	1.8×10^{-5}	4.74
Hypochlorous acid	$HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$	2.9×10^{-8}	7.54
Hydrocyanic acid	$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$	6.2×10^{-10}	9.21
Phenol	$HOC_6H_5 + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$	1.0×10^{-10}	10.00
Hydrogen peroxide	$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HO_2^-$	1.8×10^{-12}	11.74
Base		$K_b =$	p$K_b =$
Diethylamine	$(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$	6.9×10^{-4}	3.16
Ethylamine	$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$	4.3×10^{-4}	3.37
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Hydroxylamine	$HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$	9.1×10^{-9}	8.04
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.5×10^{-9}	8.82
Aniline	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	7.4×10^{-10}	9.13

Acid strength

Base strength

Acid dissociation constants.

TABLE 15.2 Acid–Dissociation Constants at 25°C

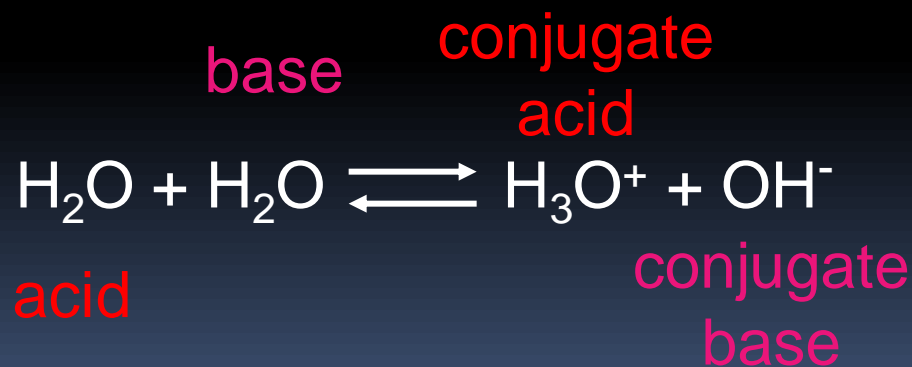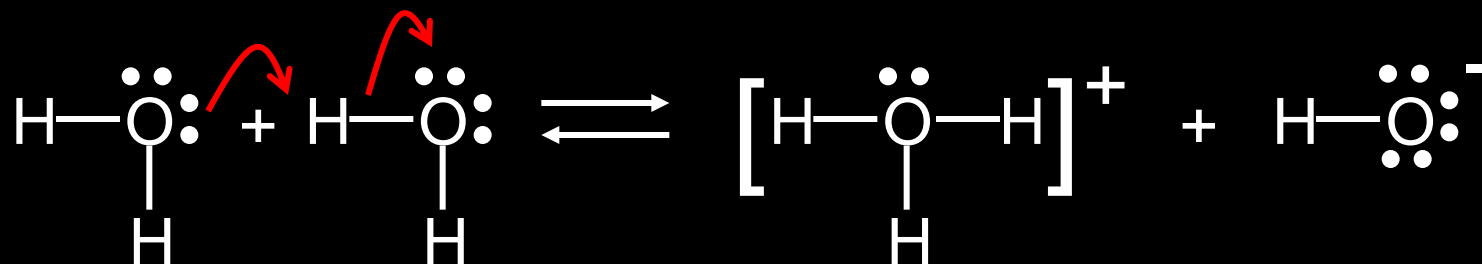|	Acid	Molecular Formula	Structural Formula*	K_a	pK_a[†]
Stronger acid	Hydrochloric	HCl	H—Cl	2×10^6	−6.3
	Nitrous	HNO_2	H—O—N=O	4.5×10^{-4}	3.35
	Hydrofluoric	HF	H—F	3.5×10^{-4}	3.46
	Acetylsalicylic (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	3.52
	Formic	HCO_2H	H—C—O—H	1.8×10^{-4}	3.74
	Ascorbic (vitamin C)	$C_6H_8O_6$		8.0×10^{-5}	4.10
	Benzoic	$C_6H_5CO_2H$		6.5×10^{-5}	4.19
	Acetic	CH_3CO_2H	CH_3—C—O—H	1.8×10^{-5}	4.74
	Hypochlorous	HOCl	H—O—Cl	3.5×10^{-8}	7.46
	Hydrocyanic	HCN	H—C≡N	4.9×10^{-10}	9.31
Weaker acid	Methanol	CH_3OH	CH_3—O—H	2.9×10^{-16}	15.54

* The proton that is transferred to water when the acid dissociates is shown in color.   [†]$pK_a = -\log K_a$.
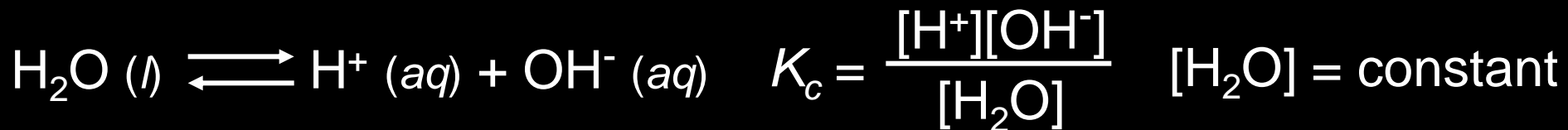
Acid-Base Properties of Water

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

autoionization of water

base

conjugate acid

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

acid

conjugate base

The Ion Product of Water

$$H_2O \ (l) \rightleftharpoons H^+ \ (aq) + OH^- \ (aq) \qquad K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c[H_2O] = K_w = [H^+][OH^-]$$

The *ion-product constant* (K_w) is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

At 25^0C
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

	Solution Is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

Basicity Constant K_b.

$$B(aq) + H_2O\ (l) \rightleftharpoons BH^+\ (aq) + OH^-\ (aq)$$
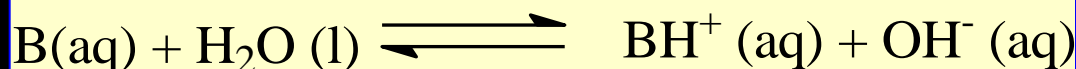
- The proton accepting strength of a base is quantified in terms of the basicity constant K_b.

- The larger the value of K_b, the stronger the base.

- If K_b is large then pK_b will be small, and the stronger will be the base.

- Solve weak base problems like weak acids **except** solve for $[OH^-]$ instead of $[H^+]$.

$$K_C = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

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

$$pK_b = -\log_{10} K_b$$

$$K_a K_b = K_W$$

$$pK_a + pK_b = pK_W$$

The pH concept.

- The best quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons $[H_3O^+]$ present in a solution.

- The $[H_3O^+]$ varies in magnitude over quite a large range in aqueous solution, typically from 1 M to 10^{-14} M.

- Hence to make the numbers meaningful $[H_3O^+]$ is expressed in terms of a logarithmic scale called the pH scale.

- The higher the $[H_3O^+]$, the more acidic the solution and the lower is the solution pH.

$$pH = -\log_{10}\left[H_3O^+\right]$$
$$\left[H_3O^+\right] = 10^{-pH}$$

$$\log(10) = \log(10^1) = 1$$
$$\log(100) = \log(10^2) = 2$$
$$\log(1000) = \log(10^3) = 3$$

Linear and logarithmic Scales.

$$\log(0.1) = \log(\frac{1}{10}) = \log(10^{-1}) = -1$$
$$\log(0.01) = \log\left(\frac{1}{10^2}\right) = \log(10^{-2}) = -2$$
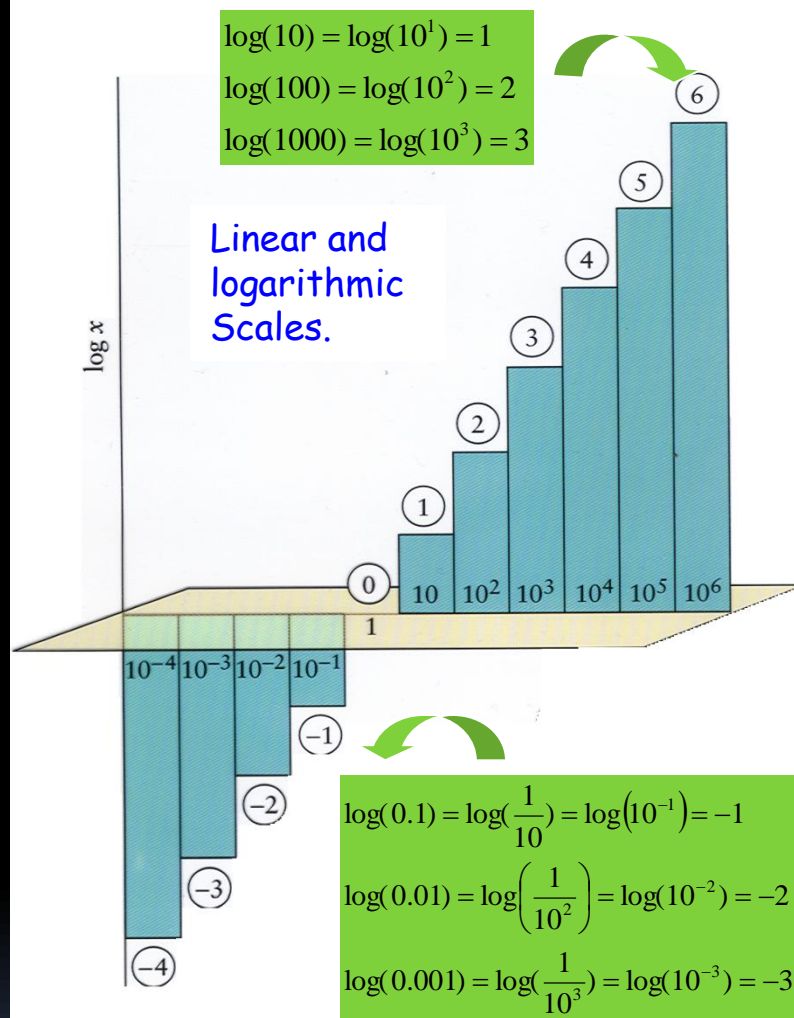$$\log(0.001) = \log(\frac{1}{10^3}) = \log(10^{-3}) = -3$$

Figure 14.8, page 515
Atkins/Jones: *Chemistry: Molecules, Matter.*   *Change.*
© 1997 by P. W. Atkins and L. L. Jones

The pH Scale.

- pH is expressed on a numerical scale from 0 to 14.
- When $[H_3O^+]$ = 1.0 M (i.e. 10^0M), pH = 0.
- When $[H_3O^+]$ = 10^{-14} M, pH = 14.
- pH value < 7 implies an acidic solution.
- pH value > 7 implies an alkaline solution.
- pH value = 7 implies that the solution is neutral.
- The definition of pH involves logarithms.
- Hence a change in one pH unit represents a change in concentration of H_3O^+ ions by a factor of 10.

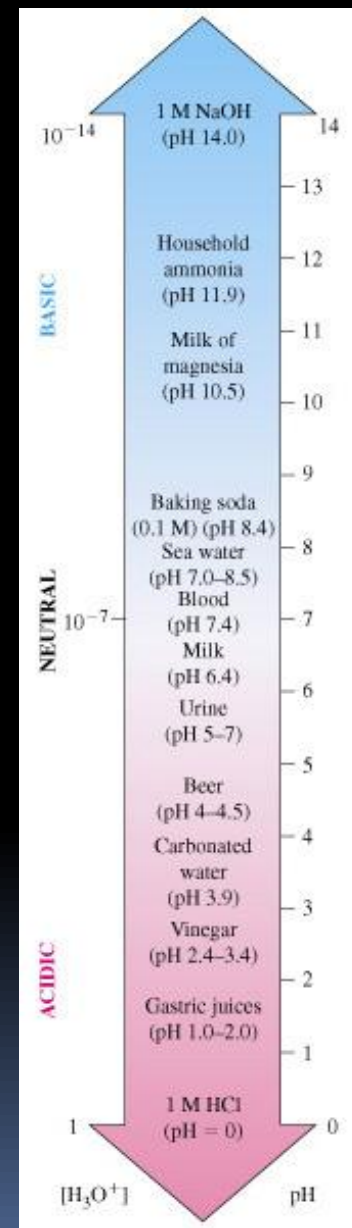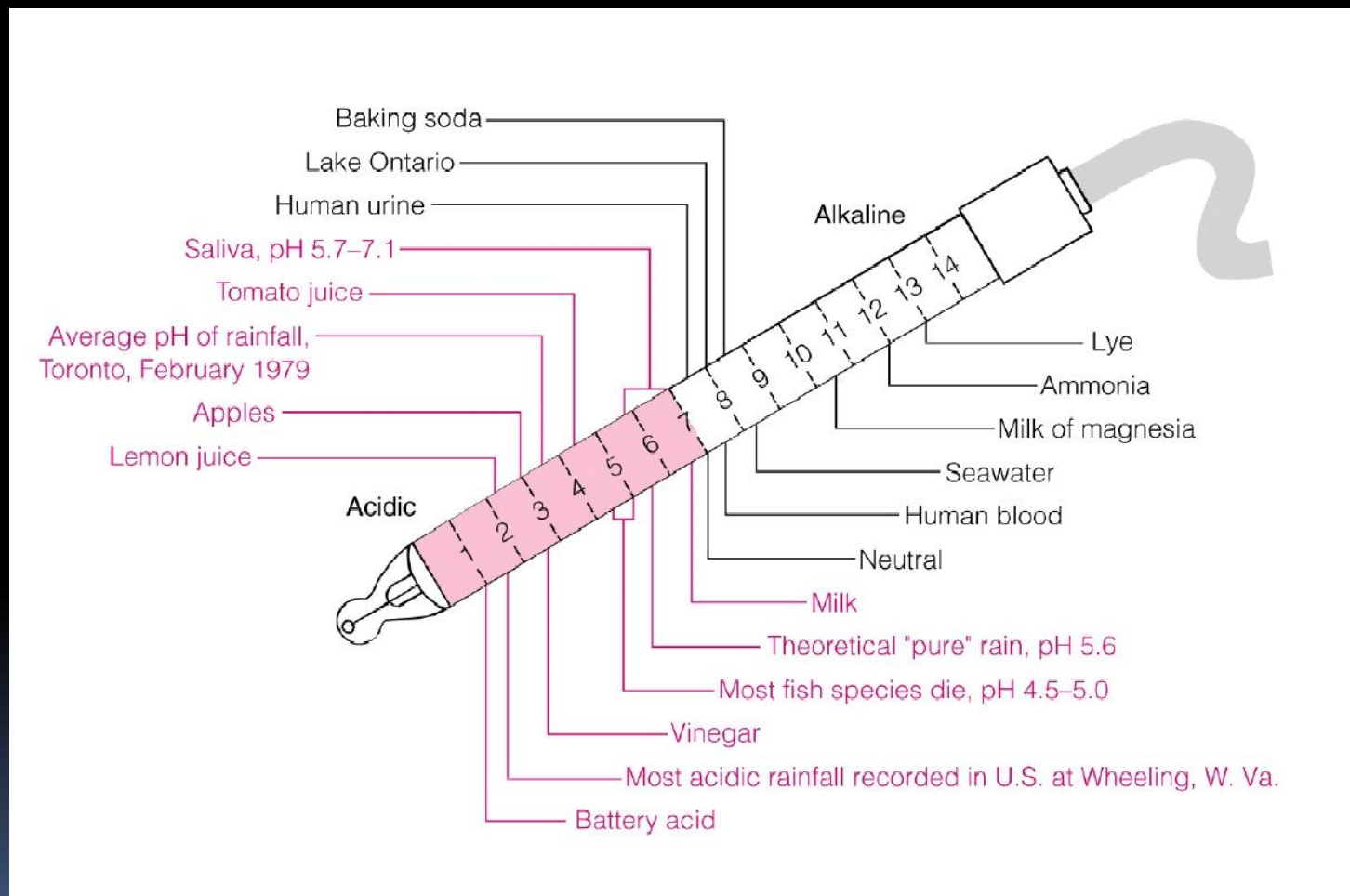$[H_3O^+]$ 1.0 M 10^{-7} M 10^{-14} M

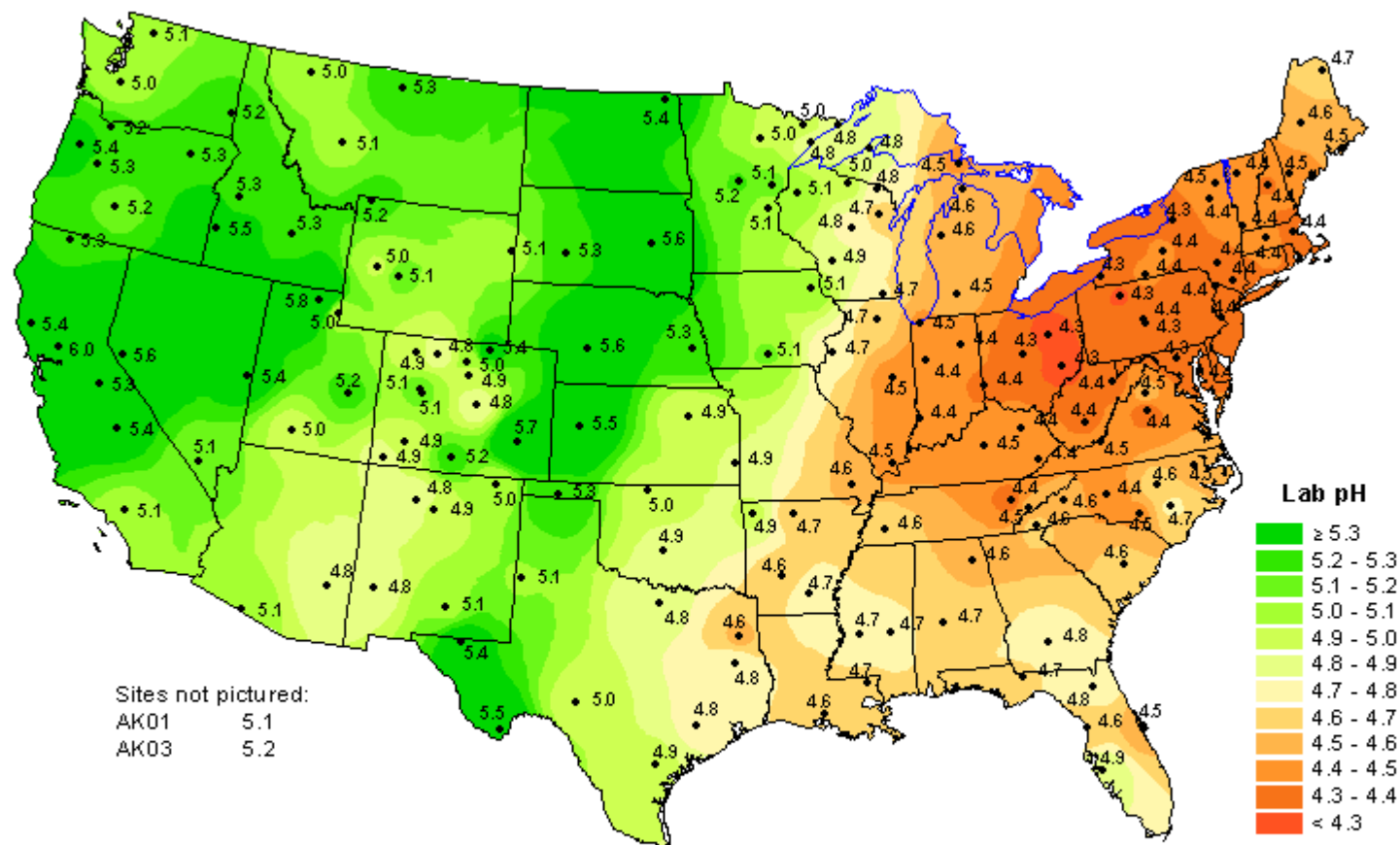0   7   14   pH
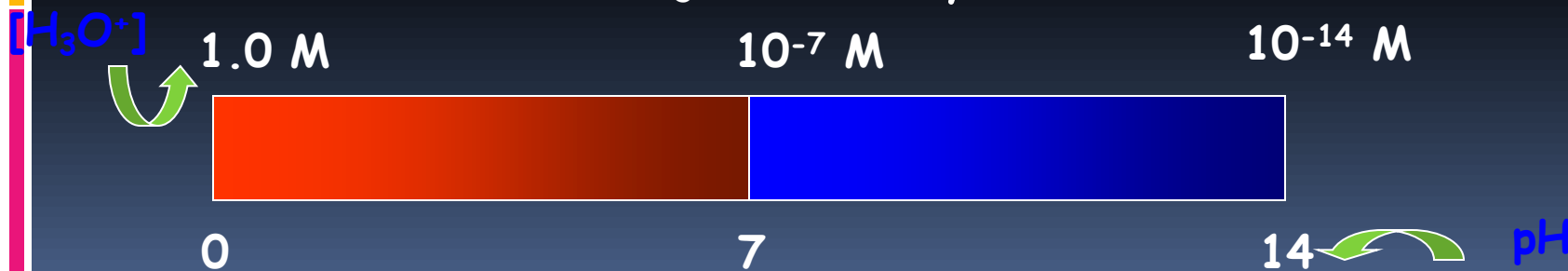
pH and pOH scales.
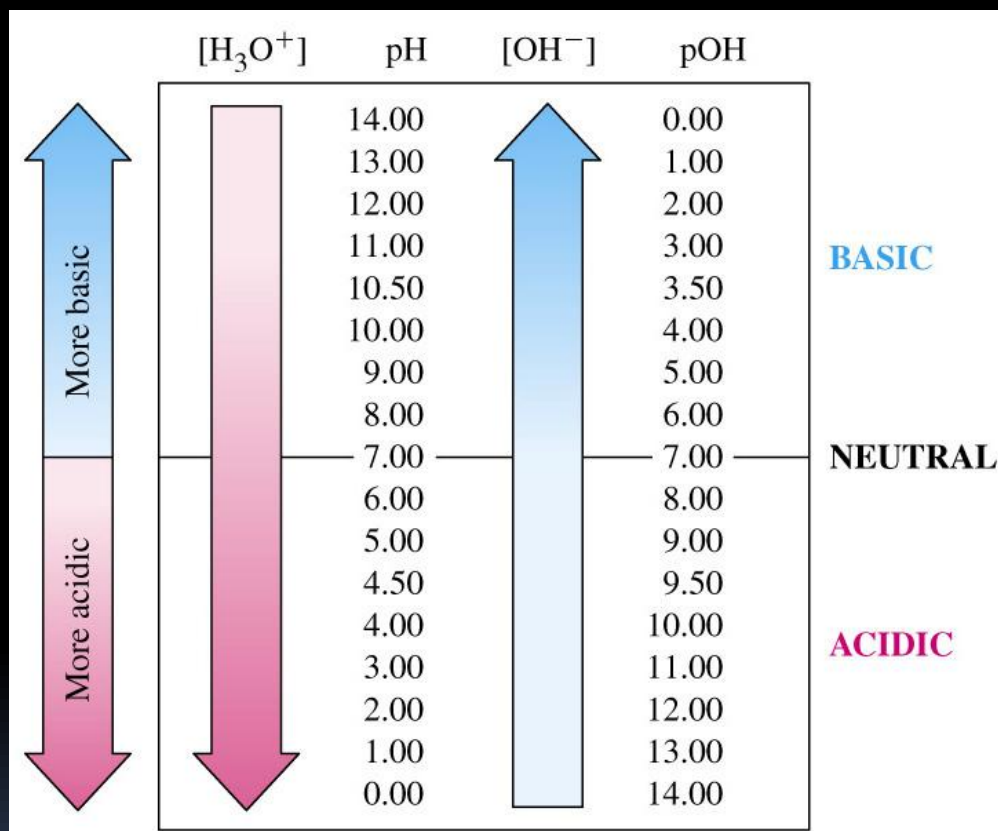
$pH = - \log[H_3O^+]$

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

Typical pH values.

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 1997

pH Measurement.

- Approximate pH of a solution determined by use of acid/base indicators.
  - Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.
  - We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.
  - This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3-10.
  - As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.

- More accurate pH values determined using an electronic instrument called a pH meter.
  - The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known $[H_3O^+]$ from the external test solution of unknown $[H_3O^+]$) located at the electrode tip.
  - This membrane potential is proportional to the pH of the test solution.
  - A digital readout of solution pH is obtained.
  - The pH meter is essentially a voltmeter connected to a chemical sensor probe which is sensitive to the concentration of hydrated protons.
  - The pH meter is an example of a potentiometric chemical sensor system. In a potentiometric chemical sensor, the measured voltage is proportional to the logarithm of the analyte concentration.
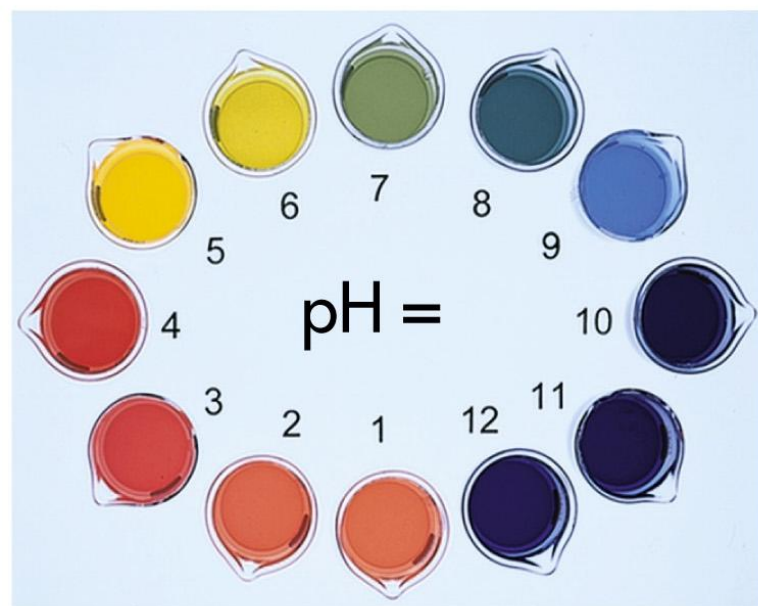
$$HIn(aq) + H_2O \rightarrow H_3O^+(aq) + In^-$$

44
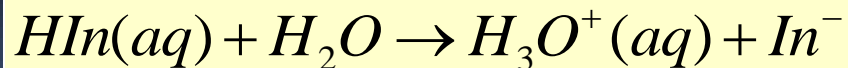
Methods for Measuring the pH of an Aqueous Solution
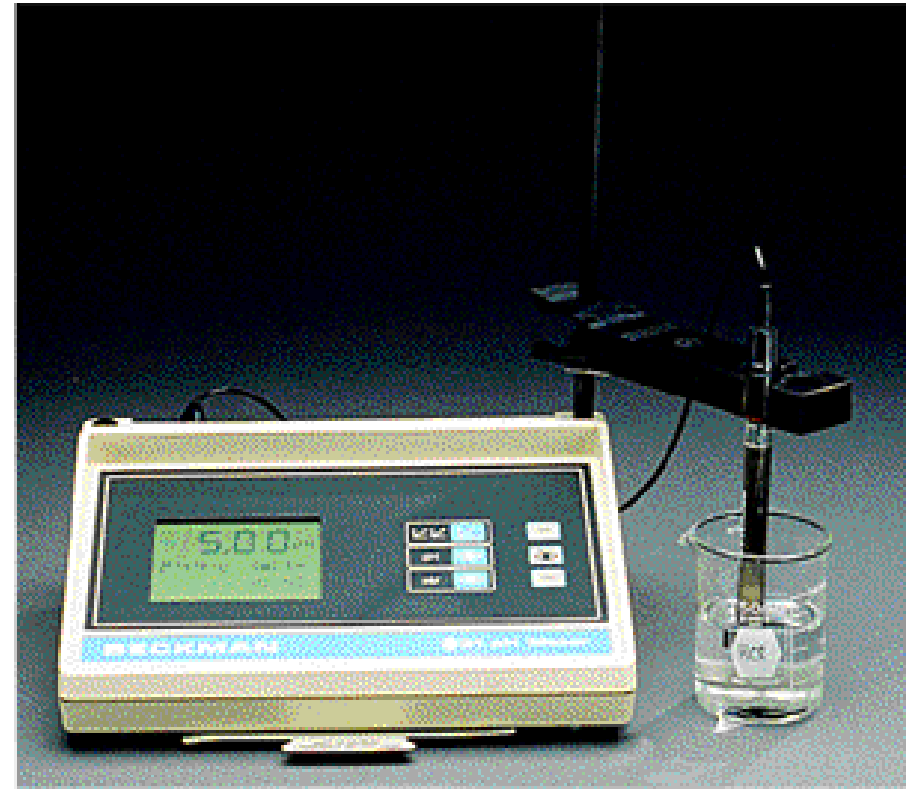
Indicators : a visual estimation of pH.

Summary. pH – A Measure of Acidity

$$pH = -\log [H^+]$$
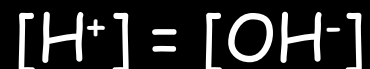
Solution Is		At 25^{0}C	
neutral	$[H^+] = [OH^-]$	$[H^+] = 1 \times 10^{-7}$	pH = 7
acidic	$[H^+] > [OH^-]$	$[H^+] > 1 \times 10^{-7}$	pH < 7
basic	$[H^+] < [OH^-]$	$[H^+] < 1 \times 10^{-7}$	pH > 7

pH ↑   [H$^+$] ↓

Titrations

In a *titration* a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

$$HA + MOH \rightarrow MA + H_2O$$
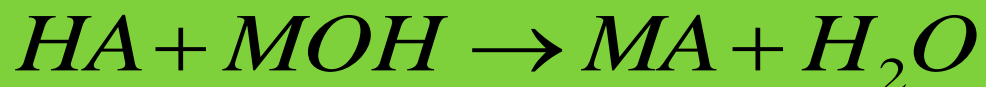
Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point
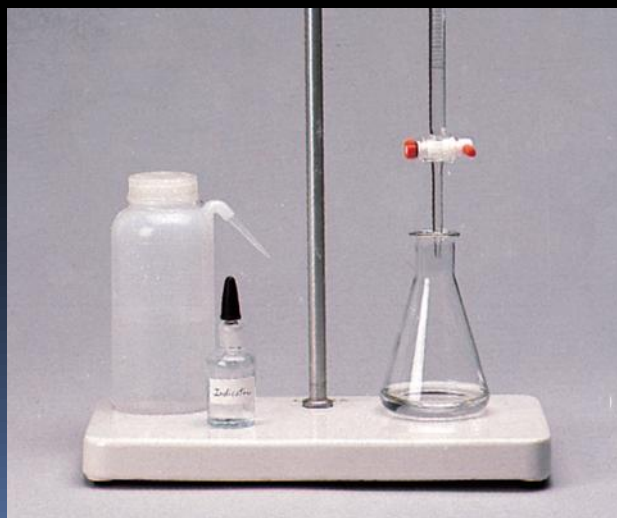
Slowly add base to unknown acid UNTIL
The indicator changes color (pink)

Strong Acid-Strong Base Titrations

$$NaOH\ (aq) + HCl\ (aq) \longrightarrow H_2O\ (l) + NaCl\ (aq)$$

$$OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$$

At equivalence point :
Amount of acid =
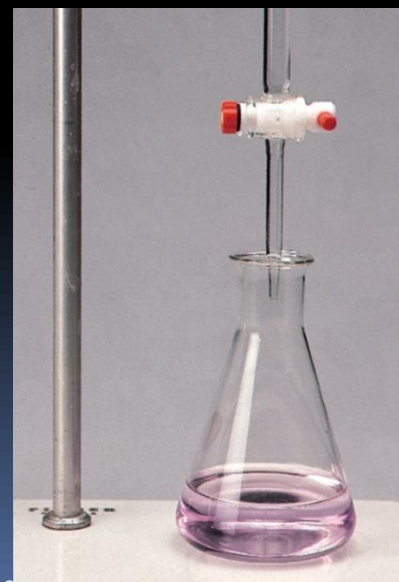Amount of base

$$n_A = n_B$$
$$c_A V_A = c_B V_B$$

0.10 M NaOH added to 25 mL of 0.10 M HCl

Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52
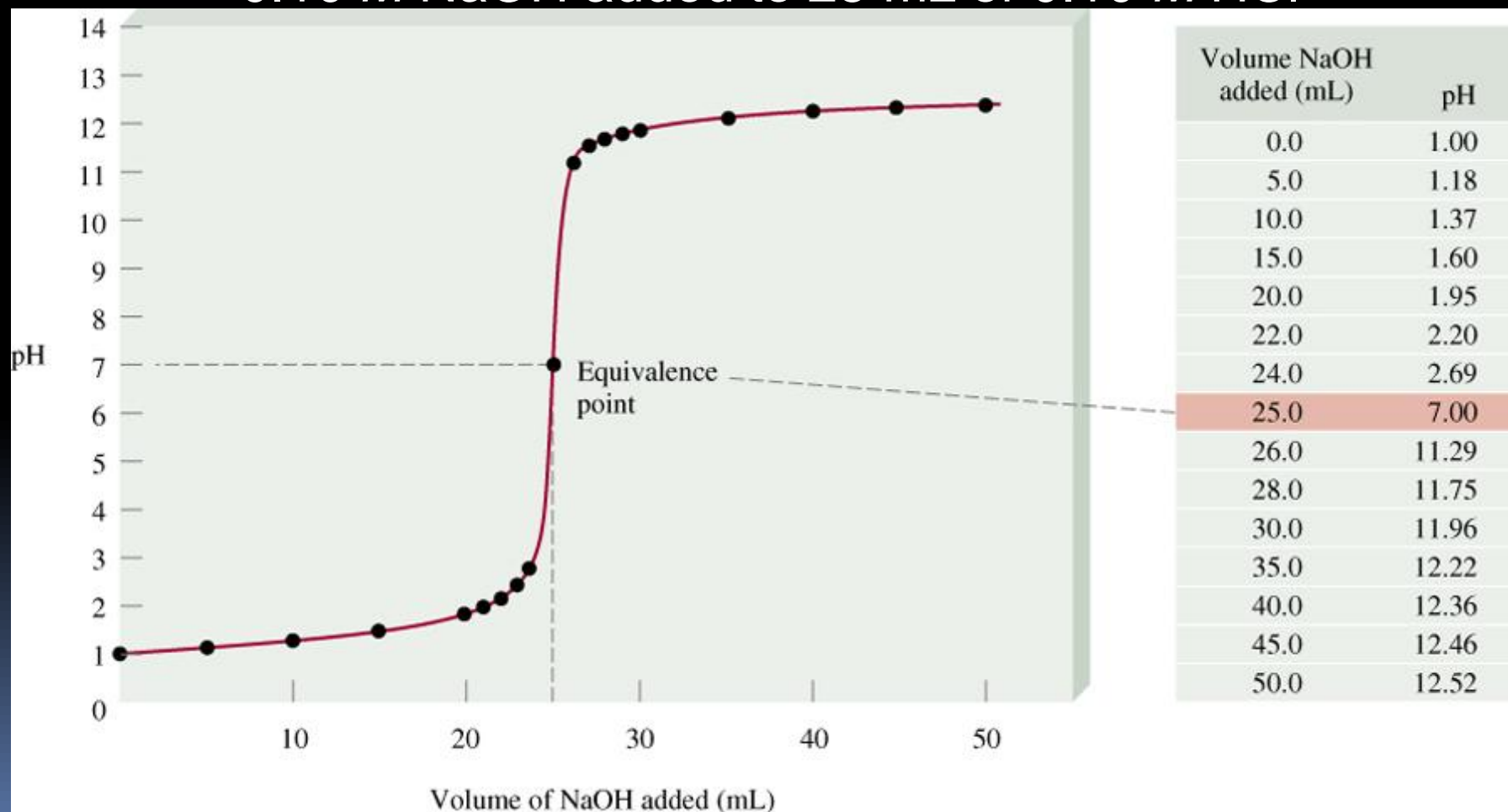
Strong Acid-Base Titration Curve

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A

Titration of 40.00 mL of 0.1000 M HCl with 0.1000 M NaOH
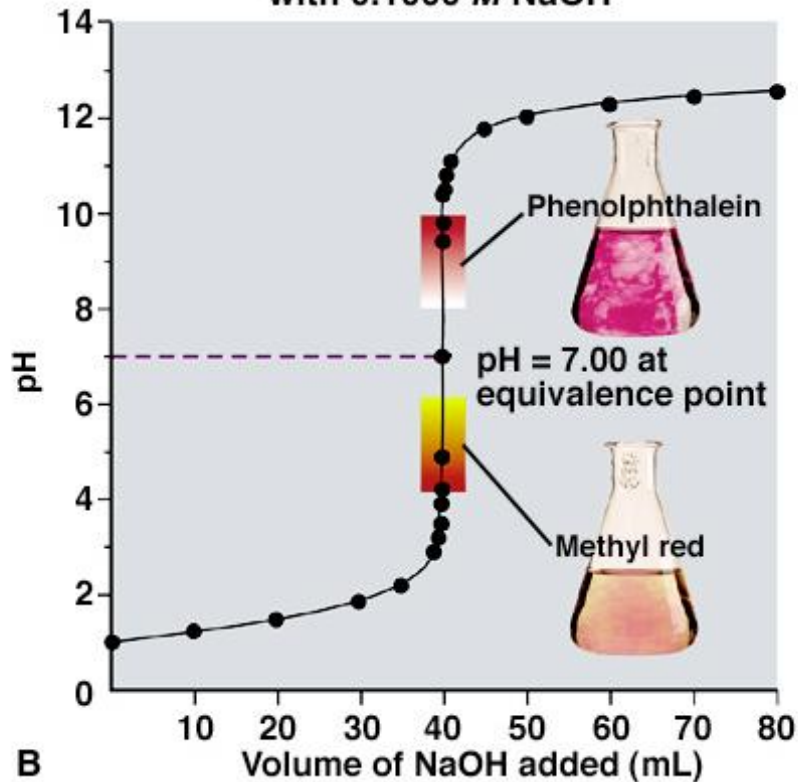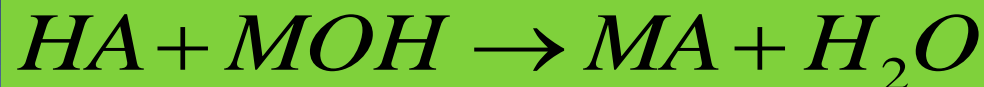
Phenolphthalein

pH = 7.00 at equivalence point

Methyl red

B

Volume of NaOH added (mL)

$$HA + MOH \rightarrow MA + H_2O$$

Weak Acid-Strong Base Titrations

$$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (l)$$

$$CH_3COOH\ (aq) + OH^-\ (aq) \longrightarrow CH_3COO^-\ (aq) + H2O\ (l)$$

At equivalence point (pH > 7):

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + CH_3COOH\ (aq)$$

Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Equivalence point

pH

Volume of NaOH added (mL)
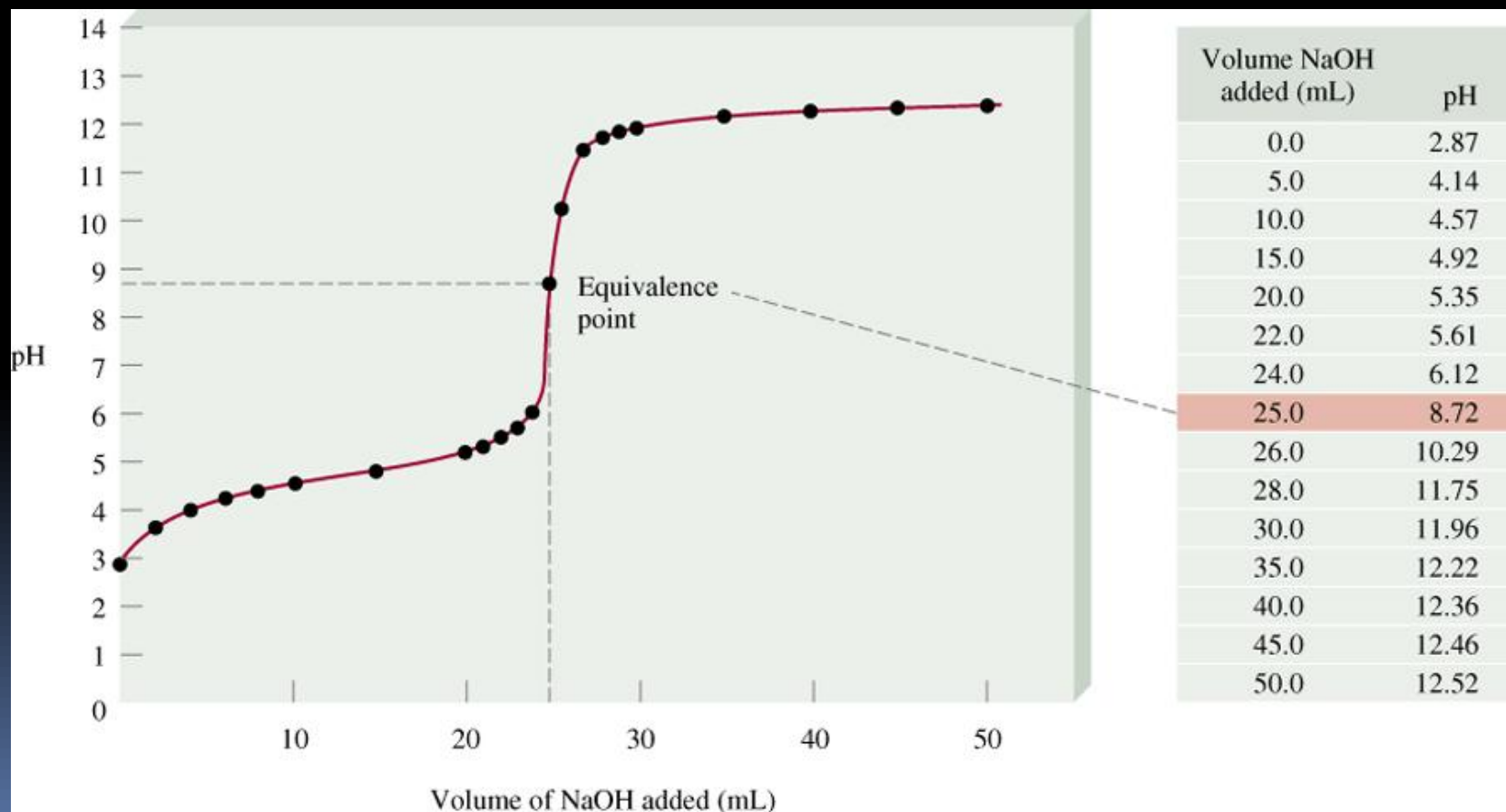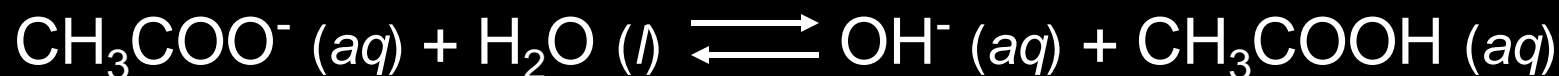
Weak Acid-Strong Base Titration Curve

Titration of 40.00 mL of 0.1000 M HPr with 0.1000 M NaOH

pK_a of HPr = 4.89

Buffer region

[HPr] = [Pr$^-$]

Phenolphthalein

pH = 8.80 at equivalence point

Methyl red

Strong acid-strong base curve

pH

Volume of NaOH added (mL)
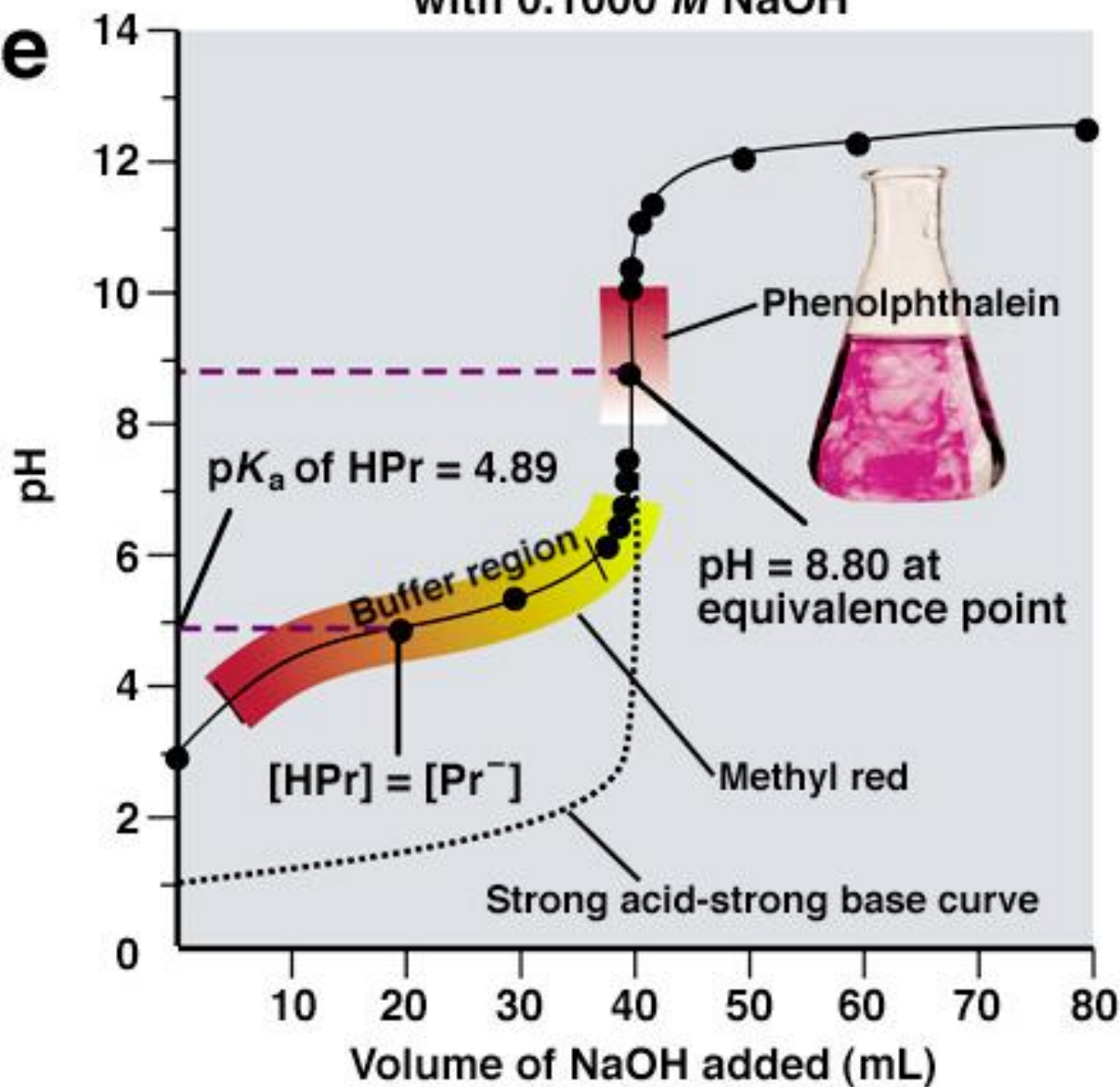
Colors and Approximate pH Range of Some Common Acid-Base Indicators
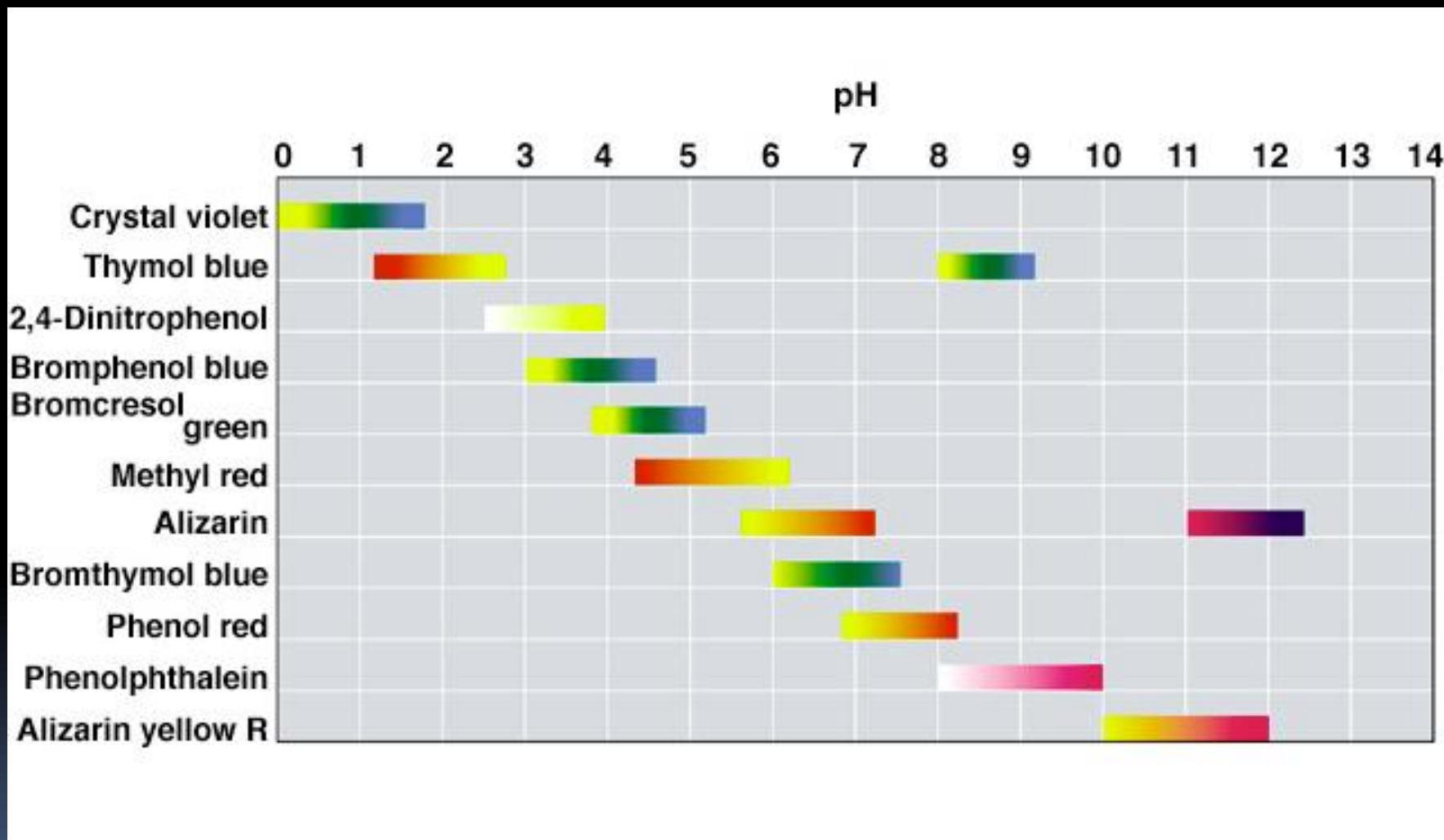
Concluding Comments

Acid/base reactions represent an example of a fundamental class of chemical reactions.

The process involves the transfer of a hydrated proton from a donor species (the acid) to an acceptor species (the base).

The degree of proton transfer can be quantified and enables a distinction between strong and weak acids/bases to be made.

The degree of acidity or alkalinity of a solution may be quantified in terms of the logarithmic pH scale. Acidic solutions have a low pH and basic solutions have a high pH.

The solution pH can be measured via use of indicators or via use of pH meter.

An acid/base reaction is termed a neutralization reaction and can be monitored by measuring the pH during the reaction.