- One day a professor was giving a big test to his students. He handed out all of the tests and went back to his desk to wait. Once the test was over, the students all handed the tests back in.

- The professor noticed that one of the students had attached a $100 bill to his test with a note saying, "A dollar per point."

- The next class, the professor handed the tests back out.

- This student got back his test and $64 change.

One day a professor was sitting alone, as usual, in his office during his office hour.

A student entered and said to the professor, "I'd do anything to get an A in your class."

"Anything?" the professor asked.

"Anything" she replied with a knowing grin.

He asked...

"would you…

study?"

Quick review of topics

- Solutions can incorporate the various states of matter
- Definitions of, calculations with molarity/molality
- Solutions can expand or contract upon dissolution, thus M is T dependent
- Dissolution can be exo- or endothermic
- Like dissolves like
- Colligative properties- specifically boiling point elevation and freezing point depression

Quick review (cont'd)

- Rate constants (little k) will be discussed in P.Chem and are experimentally determined
- Reaction rate is how fast a reaction occurs
- At equilibrium, forward and reverse rates are equal
- Reactant and product concentrations are constant at equilibrium, even though eq is DYNAMIC
- Product concentrations divided by reactant concentrations gives the equilibrium constant expression or equation (big K), with exponents equal to the stoichiometric coefficients from the balanced equation (pure solids and liquids do not appear)
- Size of K (either in terms of concentration or pressure) gives the extent of reaction ("how far to the left or right the reaction lies")
- The reaction quotient Q starts at zero and goes to K
- Use LeChatelier to predict effects of changing P, V or T
- Catalysts (enzymes, biologically) lower activation energy and speed up reactions… they do not effect eq

Professor K

Acids and bases

Acids and bases expanded

- Must know 3 definitions
- Must know common strong/weak acids/bases
- Using your knowledge of acid-base reactions and reaction equilibria, mathematical expressions of acid-base equilibria can be given

Review

- Remember, Arrhenius said acids donated protons and bases donated hydroxide ions
- Bronsted said that acids are proton donors and bases are proton acceptors
- Bronsted theory required no water
- Lewis definitions involve electron pairs
  - A Lewis acid is an electron pair acceptor
    - Electrophile ("electron-loving")
  - A Lewis base is an electron pair donor
    - Nucleophile ("nucleus-loving")

Conjugate acid-base pairs are apparent in an acid-base reaction at equilibrium

- Ex. $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
- NH_4^+ is the conjugate acid of the base NH_3
- OH^- is the conjugate base of the acid H_2O
- So a conjugate base is an acid minus a proton
- And a conjugate acid is a base plus a proton
- A substance that can act as both an acid and a base is called amphoteric (or amphiprotic)

Ionization of HCl

- $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
- Acid + Base $\rightarrow$ conj. acid + conj. base

K_a and K_b

- The K for an acid-base equilibrium is called either the acid or base ionization constant (depending on the molecules involved)
- Strong acids have a large K_a and strong bases have a large K_b (why???)
- A strong acid has a weak conjugate base (why???)
- A strong base has a weak conjugate acid
- Explanations of the acidity/basicity of salts tend to be longwinded and unnecessary... what do you *know* to determine whether NH_4Cl and Na_2CO_3 are acidic or not?

Long-windedness

- Salts of strong acids and strong bases form neutral solutions of salt: NaCl, KNO_3
- Salts of weak acids and strong bases form basic solutions, since the weak acid will have a relatively strong conjugate base: KNO_2, NaClO
- Salts of strong acids and weak bases form acidic solutions: NH_4NO_3
- Salts of weak acids and weak bases form solutions that may be acidic, basic, or neutral; it depends on the relative strengths of the cations and anions: NH_4NO_2, CH_3COONH_4

Factors affecting acid strength for binary acids

- Bond strength

- Atomic radius

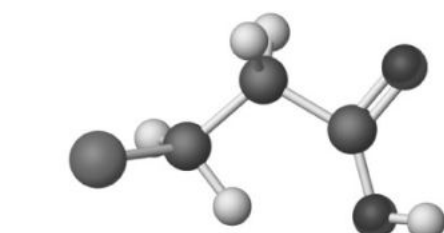- Ionic or covalent character
  - electronegativity differences

Factors affecting acid strength for other acids and bases

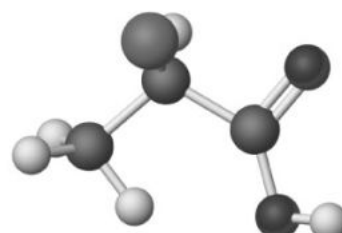- Electron Withdrawing Groups (EWG's) attached to carboxylic acids
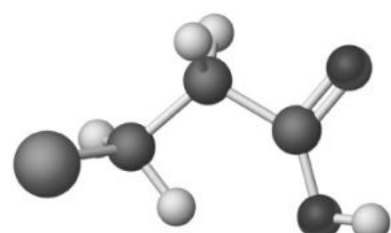
$I\!-\!CH_2CH_2COOH$
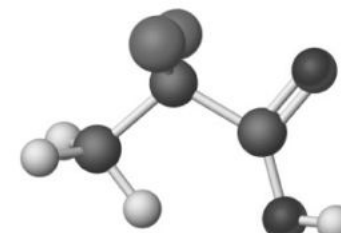3-Iodopropanoic acid
$K_a = 8.3 \times 10^{-5}$ $<$

$Cl\!-\!CH_2CH_2COOH$
3-Chloropropanoic acid
$K_a = 1.0 \times 10^{-4}$ $<$

$CH_3CHClOOH$
2-Chloropropanoic acid
$K_a = 1.4 \times 10^{-3}$ $<$

CH_3CCl_2COOH
2,2-Dichloropropanoic acid
$K_a = 8.7 \times 10^{-3}$

Increasing acid strength →

- ## EWG's on amines
  - Aromatic amines are much weaker bases than aliphatic amines.
  - This is due in part to the fact that the π electrons in the benzene ring of an aromatic molecule are *delocalized* and can involve the nitrogen atom's lone-pair electrons in the resonance hybrid.
  - As a result, the lone-pair electrons are much less likely to accept a proton.
  - Electron-withdrawing groups on the ring further diminish the basicity of aromatic amines relative to aniline.

Self-ionization of water

- Even pure water conducts "some" electricity. This is due to the fact that water auto-ionizes:

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

- The equilibrium constant for this process is called the **ion product of water** (K_w)

- At 25^oC, $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$

- This equilibrium constant is very important because it applies to **all aqueous solutions**- acids, bases, salts, and nonelectrolytes- not just to pure water.

The pH scale

- Concentration of H_3O^+ can vary over a wide range in aqueous solution, from about 10 M to about 10^{-14} M.

- A more convenient expression for H_3O^+ is **pH**. Lowercase "p" and uppercase "H"

- $pH = -\log [H_3O^+]$ and so $[H_3O^+] = 10^{-pH}$

- The "negative logarithm" function of pH is so useful that it has been applied to other species and constants.

  pOH $= -\log [OH^-]$ and so $[OH^-] = 10^{-pOH}$

  pK_w $= -\log K_w$

- At 25 °C, $pK_w = 14.00$

- $pK_w = pH + pOH = 14.00$

- Calculations

- Polyprotic acids – values of K_a decrease successively for a given polyprotic acid. $K_{a1} > K_{a2} > K_{a3}$, etc.
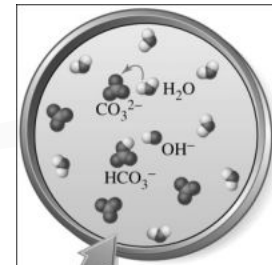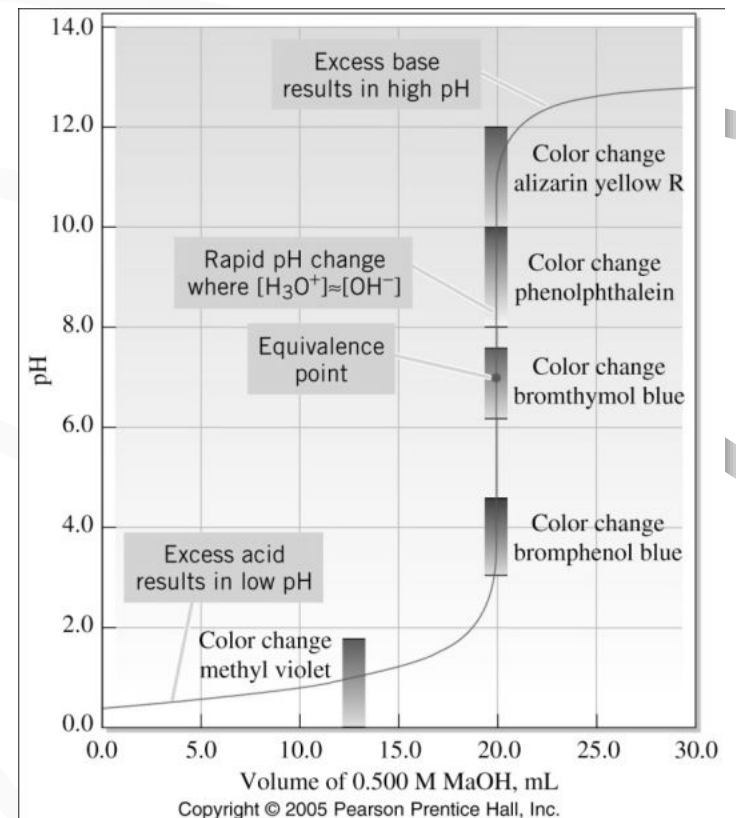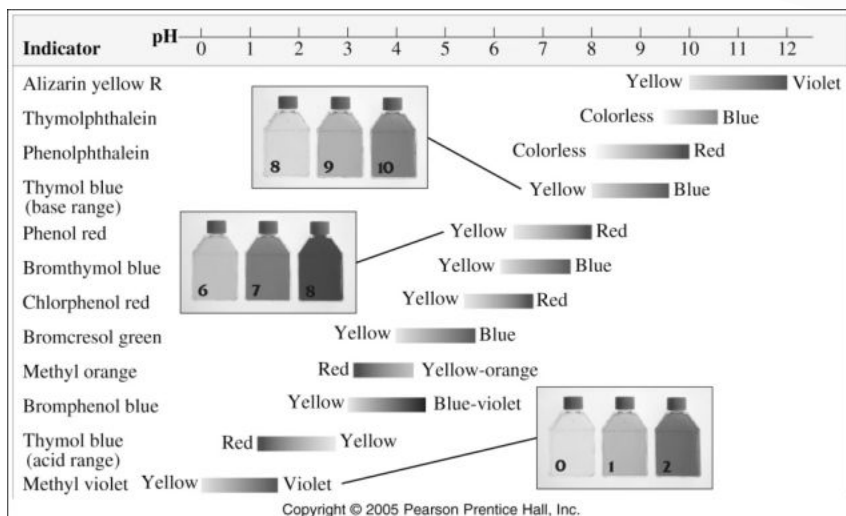
The pH scale (cont'd)
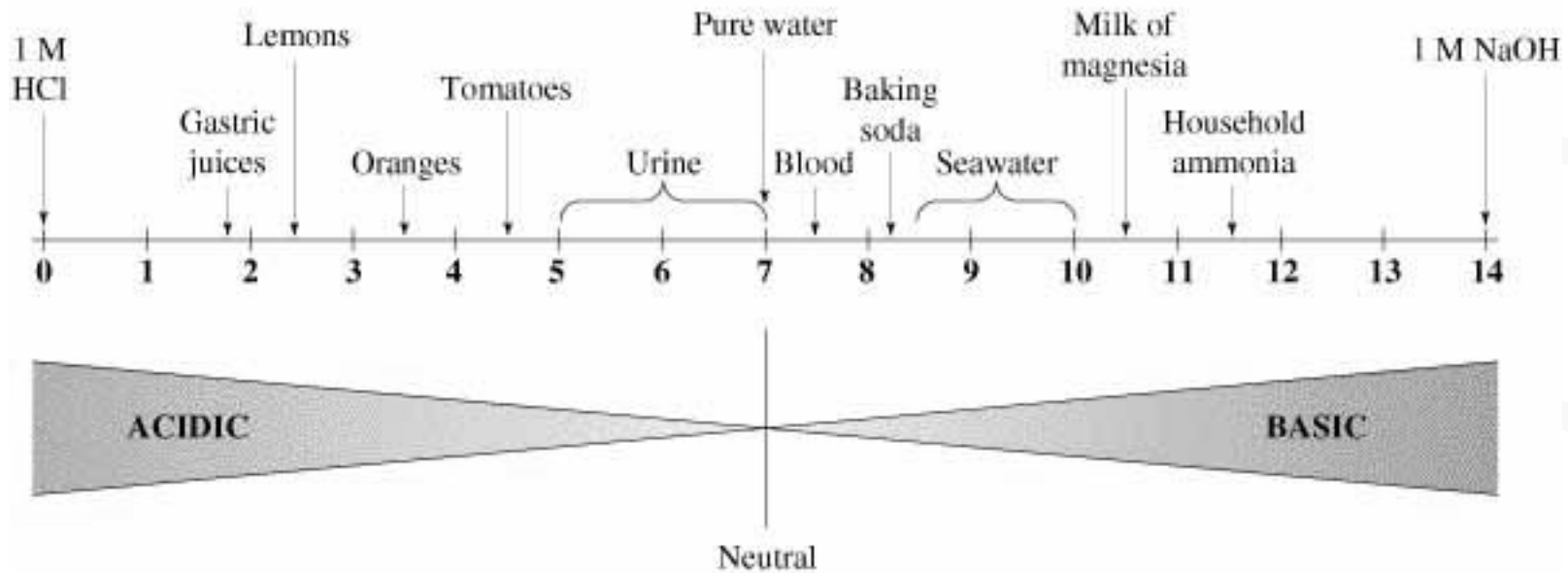
Other topics

- Ions as acids and bases
- Common ion effect (LeChatelier revisited)
- Buffers (use in lab)
- Indicators (use in lab)
- Neutralization reactions and titration curves (use in lab)

The common ion effect

- The suppression of the ionization of a weak acid or base by the presence of a common ion from a strong electrolyte.

Buffer solutions

- Many industrial and biochemical reactions-especially enzyme-catalyzed reactions- are sensitive to pH.
- To work with such reactions, we often need a solution that maintains a nearly constant pH.
- A **buffer solution** is a solution that changes pH *only slightly* when small amounts of a strong acid or base are added.
- A buffer contains significant concentrations of **both**:
  - a weak acid and its conjugate base, or
  - a weak base and its conjugate acid.

Buffer solutions (cont'd)

- The acid component of a buffer neutralizes small amounts of OH$^-$ added, forming the weaker conjugate base, which has little effect on pH:

$$HA + OH^- \rightarrow H_2O + A^-$$
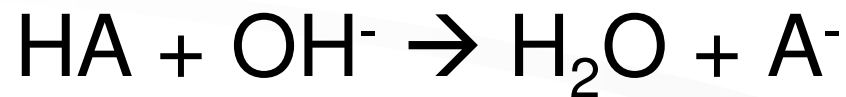
- The base component neutralizes small amounts of H$^+$ added, forming the weaker conjugate acid, which has little effect on pH:

$$A^- + H^+ \rightarrow H_2O + HA$$

- Pure water has no buffering capacity.

An equation for buffer solutions

- In certain applications, there is a need to repeat the calculations of the pH of buffer solutions many times. This can be accomplished with a single, simple equation, which has some limitations.
- The Henderson-Hasselbalch equation:

$$pH = pK_a + \log ([conj\ base]/[weak\ acid])$$

- To use this equation, the ratio of base to acid must be between 0.10 and 10, and both concentrations must exceed K_a by a factor of 100 or more.
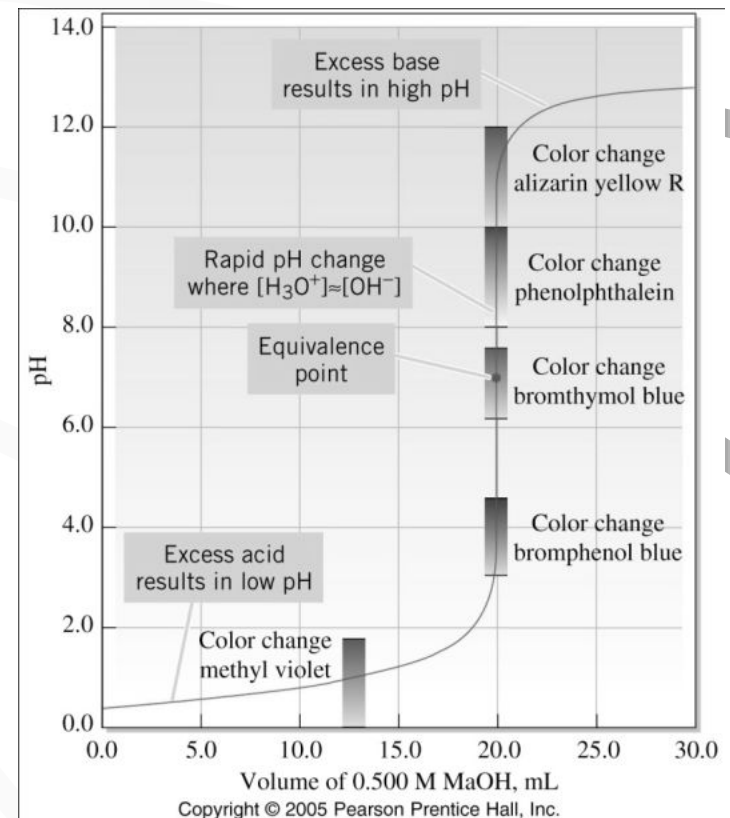
Acid-base indicators

- An acid-base indicator is a weak acid or base (important info for lab use!) often used when a precise pH reading isn't necessary.
- The acid form (HA) of the indicator has one color, while the conjugate base (A^-) has a different color. One of the "colors" may be colorless.
- In an acidic solution, [H^+] is high (low pH). Because H^+ is the common ion, it suppresses the ionization of the indicator acid, and we see the color of HA.
- In a basic solution, [OH^-] is high, and it reacts with HA, forming the color of A^-.

Different indicators have different K_a and change colors at different pH

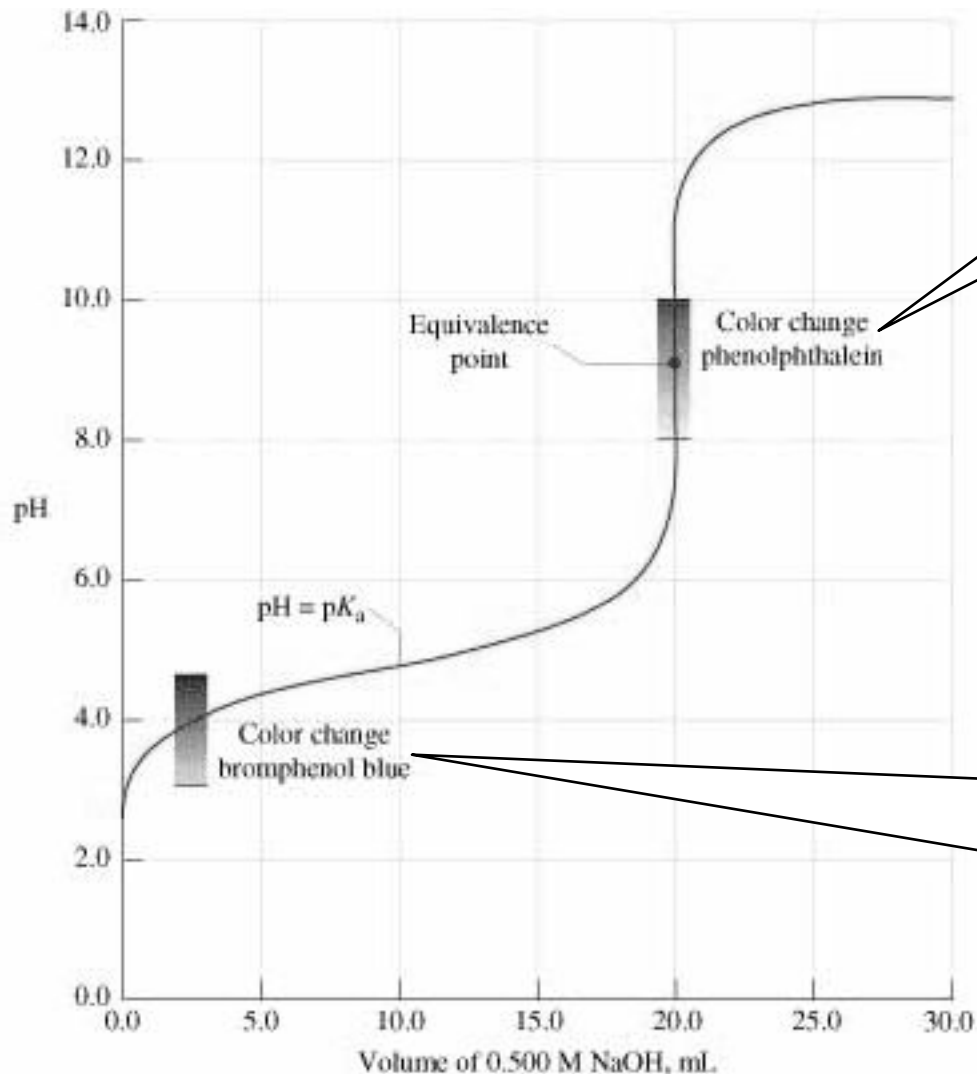Copyright © 2005 Pearson Prentice Hall, Inc.
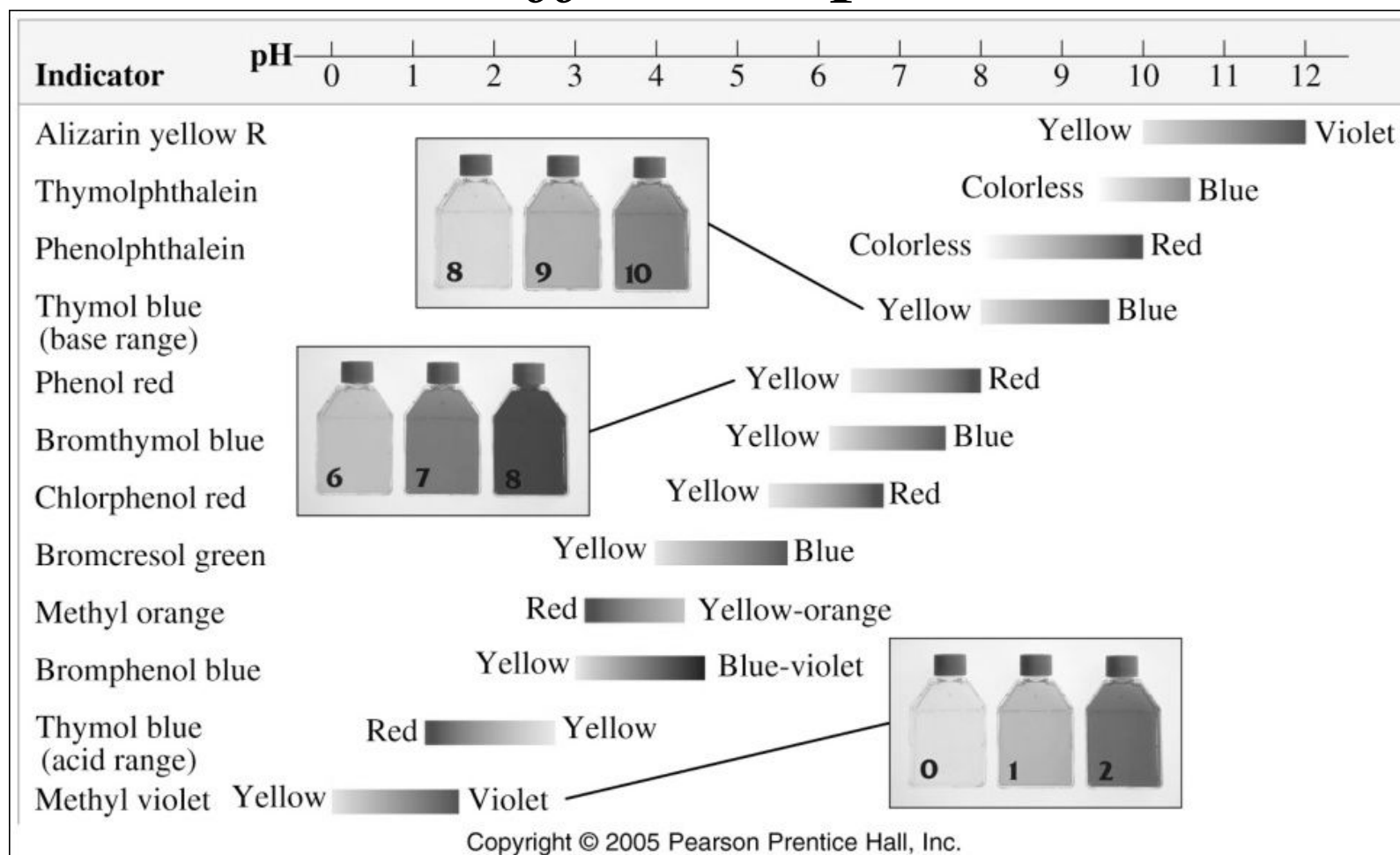
Neutralization reactions

- At the equivalence point in an acid–base titration, the acid and base have been brought together in precise stoichiometric proportions.
- The endpoint is the point in the titration at which the indicator changes color.
- Ideally, the indicator is selected so that the endpoint and the equivalence point are very close together.
- The endpoint and the equivalence point for a neutralization titration can be best matched by plotting a titration curve, a graph of pH versus volume of titrant.

Excess base results in high pH

Color change alizarin yellow R

Rapid pH change where [H₃O⁺]≈[OH⁻]

Color change phenolphthalein

Equivalence point

Color change bromthymol blue

Color change bromphenol blue

Excess acid results in low pH

Color change methyl violet

Volume of 0.500 M MaOH, mL

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Titration curve-
weak acid with strong base

The equivalence point pH is NOT 7.0... why not?

Bromphenol blue is OK for a strong acid/strong base titration, but it changes color too early to be useful here.