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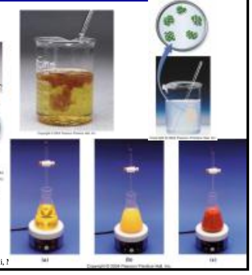
Chapter Four

Chemical Reactions in Aqueous Solutions



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4.1 Some Electrical Properties of Aqueous Solutions

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Electrostatic Forces

- Unlike charges (+ and –) attract one another.
- Like charges (+ and +, or – and –) repel one another.

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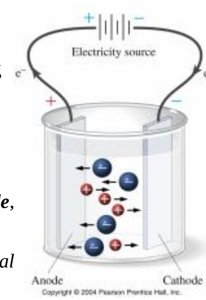
Conduction Illustrated

- Electric current is a flow of charged particles.
- One type of current is electrons flowing through a wire, from ***cathode*** (negative electrode) to ***anode*** (positive electrode).
- Another type of current: anions and cations moving through a solution as shown here. Cations move to the ***cathode***, anions move to the ***anode***.
- Of course, an external source of *potential* (voltage) is required in either case!



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Arrhenius's Theory of Electrolytic Dissociation

- Why do some solutions conduct electricity?
- An early hypothesis was that electricity *produced* ions in solution, and those ions allowed the electricity to flow.
- Arrhenius's theory:
  - Certain substances ***dissociate*** into cations and anions when dissolved in water.
  - The ions ***already present in solution*** allow electricity to flow.

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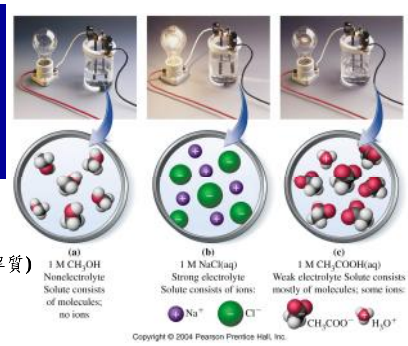
Electrolytic Properties of Aqueous Solutions



- ***Electrolytes*(電解質)** dissociate to produce ions.

The more the electrolyte dissociates, the more ions it produces.

Types of Electrolytes(電解質)

- A ***strong electrolyte*(強電解質)** dissociates completely.
  - A strong electrolyte is present in solution almost exclusively as ***ions***.
  - Strong electrolyte solutions are good conductors.
- A ***nonelectrolyte*(非電解質)** does not dissociate.
  - A nonelectrolyte is present in solution almost exclusively as ***molecules***.
  - Nonelectrolyte solutions do not conduct electricity.
- A ***weak electrolyte* (弱電解質)** dissociates partially.
  - Weak electrolyte solutions are poor conductors.
  - Different weak electrolytes dissociate to different extents.

Is it a strong electrolyte, a weak electrolyte, or a nonelectrolyte?

- Strong electrolytes include:
  - Strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$)
  - Strong bases (IA and IIA hydroxides)
  - Most water-soluble ionic compounds
- Weak electrolytes include:
  - Weak acids and weak bases
  - A few ionic compounds
- Nonelectrolytes include:
  - Most molecular compounds
  - Most organic compounds (most of them are molecular)

How do we tell whether an acid (or base) is *weak*?

Calculating Ion Concentrations in Solution

- In 0.010 M Na_2SO_4:
  - two moles of Na^+ ions are formed for each mole of Na_2SO_4 in solution, so $[Na^+]$ = 0.020 M.
  - one mole of SO_4^{2-} ion is formed for each mole of Na_2SO_4 in solution, so $[SO_4^{2-}]$ = 0.010 M.
- An ion can have only ***one*** concentration in a solution, even if the ion has two or more sources.

Example 4.1

Calculate the molarity of each ion in an aqueous solution that is 0.00384 M Na_2SO_4 and 0.00202 M NaCl. In addition, calculate the total ion concentration of the solution.

4.2 Reactions of Acids and Bases

Reactions of Acids and Bases: Strong and Weak Acids

- ***Strong acids*** are strong electrolytes; completely ionized in water.

  In water: $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

  No HCl in solution, only H^+ and Cl^- ions.

- **Weak acids** are weak electrolytes. ***Some*** of the dissolved molecules ionize; the rest remain as molecules.

  In water: $CH_3COOH(l) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

  Just a little H^+ forms.

Some acids have more than one ionizable hydrogen atom. They ionize in "steps" (more in Chapter 15).

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

Strong and Weak Bases

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- ***Strong bases***: Most are ionic hydroxides (Group IA and IIA, though some IIA hydroxides aren't very soluble).
- ***Weak bases***: Like weak acids, they ionize partially. Ionization process is *different.*
- Weak bases *form* OH^- by accepting H^+ from water …

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

methylamine — methylammonium ion

Most of the weak base remains in the molecular form.

Just a little OH^- forms.

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Common Strong Acids and Strong Bases

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Table 4.1 Common Strong Acids and Strong Bases

Acids		Bases	
Binary Hydrogen Compounds	Oxoacids	Group 1A hydroxides	Group 2A hydroxides
HCl	HNO_3	LiOH	$Mg(OH)_2$
HBr	H_2SO_4[a]	NaOH	$Ca(OH)_2$
HI	$HClO_4$	KOH	$Sr(OH)_2$
		RbOH	$Ba(OH)_2$
		CsOH	

[a] H_2SO_4 is a strong acid in its first ioniza… weak in its second ionization step.

A pragmatic method of determining whether an acid is weak … just learn the strong acids!

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Acid–Base Reactions: Neutralization

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- In the reaction of an acid with a base, the identifying characteristics of each "cancel out."
- ***Neutralization*(中和反應)** is the (usually complete) reaction of an acid with a base.
- The products of this neutralization are water and a ***salt***.

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Acid–Base Reactions: Net Ionic Equations

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$$HCl + NaOH \rightarrow H_2O + NaCl$$

- In the reaction above, the HCl, NaOH, and NaCl all are strong electrolytes and dissociate completely.
- The actual reaction occurs between ***ions***.

Na^+ and Cl^- are *spectator* ions.

$$H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \rightarrow H_2O + \cancel{Na^+} + \cancel{Cl^-}$$

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

A ***net ionic*** equation shows the species actually involved in the reaction.

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Example 4.2

Barium nitrate, used to produce a green color in fireworks, can be made by the reaction of nitric acid with barium hydroxide. Write **(a)** a complete-formula equation, **(b)** an ionic equation, and **(c)** a net ionic equation for this neutralization reaction.

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Indicators(指示劑)

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- ***Indicators*** are commonly used to tell when a neutralization is complete, or if a solution is acidic or basic. ***Phenol red*** is …

… yellow in acidic solution …

… orange in neutral solution …

… and red in basic solution.

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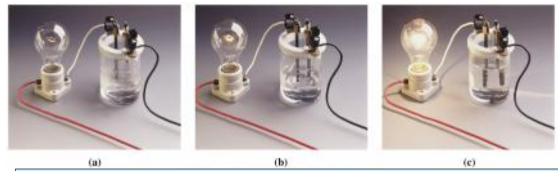
Acid–Base Reactions: Additional Examples

Water-insoluble hydroxides are used as antacids.

Baking soda, when acidified, forms carbon dioxide gas that causes cakes, cookies, and "quick breads" to rise.

Example 4.3 A Conceptual Example

Explain the observations illustrated in Figure 4.6.



Change in electrical conductivity as a result of a chemical reaction

(a) When the beaker contains a 1 M solution of acetic acid, CH_3COOH, the bulb in the electric circuit glows only very dimly. **(b)** When the beaker contains a 1 M solution of ammonia, NH_3, the bulb again glows only dimly. **(c)** When the two solutions are in the same beaker, the bulb glows brightly. What happens when the two solutions are mixed is described in Example 4.3.

4.3 Reactions that Form Precipitates

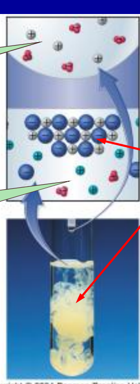
Reactions that Form Precipitates

- There are limits to the amount of a solute that will dissolve in a given amount of water.
- If the maximum concentration of solute is less than about 0.01 M, we refer to the solute as *insoluble* in water.
- When a chemical reaction forms such a solute, the insoluble solute comes out of solution and is called a ***precipitate***.

Silver Iodide Precipitation

A solution containing silver ions and nitrate ions, when added to …

… a solution containing potassium ions and iodide ions, forms …



… a precipitate of silver iodide.

What is the net ionic equation for the reaction that has occurred here? (Hint: what species actually reacted?)

Table 4.3 General Guidelines for the Water Solubilities of Common Ionic Compounds

Almost all nitrates, acetates, perchlorates, group 1A metal salts, and ammonium salts are *SOLUBLE*.

Most chlorides, bromides, and iodides are *SOLUBLE*. Exceptions: those of Pb^{2+}, Ag^{+}, and Hg_2^{2+}.

Most sulfates are *SOLUBLE*. Exceptions: those of Sr^{2+}, Ba^{2+}, Pb^{2+}, and Hg_2^{2+} ($CaSO_4$ is slightly soluble).

Most carbonates, hydroxides, phosphates, and sulfides are *INSOLUBLE*. Exceptions: ammonium and group 1A metal salts of any of those anions are soluble; hydroxides and sulfides of Ca^{2+}, Sr^{2+}, and Ba^{2+} are slightly to moderately soluble.

- With these guidelines we can predict precipitation reactions.
- When solutions of sodium carbonate and iron(III) nitrate are mixed, a precipitate will form.
- When solutions of lead acetate and calcium chloride are mixed, a precipitate will form.

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沈澱反應規則

沈澱 – 由兩種不同溶液的陽離子與陰離子相互作，不可溶的固體將會被分離出來

- 所有鹼金屬(IA族)及銨(NH_4^+)化合物均具可溶性
- 所有含NO_3^-(硝酸根)、 ClO_3^-(氯酸根)、 ClO_4^-(過氯酸根)的化合物均可溶
- 除IA族之氫氧化物、$Ba(OH)_2$為可溶、$Ca(OH)_2$為微溶外，其餘之氫氧化物(OH^-)均不可溶
- 多數氯化物(Cl^-)、溴化物(Br^-)、碘化物(I^-)是可溶，但含Ag^+、Hg_2^{+2}、Pb^{+2}例外
- 所有碳酸根(CO_3^{-2})、磷酸根(PO_4^{-3})及硫化物(S^{-2})均為不溶性
- 大多數SO_4^{-2}(硫酸根)為可溶性，但$CaSO_4$(硫酸鈣)及Ag_2SO_4(硫酸銀)為微溶；$BaSO_4$(硫酸鋇)、$HgSO_4$(硫酸汞)及$PbSO_4$(硫酸鉛)為不溶性

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Example 4.4

Predict whether a precipitation reaction will occur in each of the following cases. If so, write a net ionic equation for the reaction.

(a) $Na_2SO_4(aq) + MgCl_2(aq) \rightarrow ?$

(b) $(NH_4)_2S(aq) + Cu(NO_3)_2(aq) \rightarrow ?$

(c) $K_2CO_3(aq) + ZnCl_2(aq) \rightarrow ?$

Example 4.5

A Conceptual Example

Figure 4.8 shows that the dropwise addition of $NH_3(aq)$ to $FeCl_3(aq)$ produces a precipitate. What is the precipitate?

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Table 4.4 Some Precipitation Reactions of Practical Importance

Reaction in Aqueous Solution	Application
$Al^{3+}(aq) + 3\,OH^-(aq) \longrightarrow Al(OH)_3(s)$	Water purification. (The gelatinous precipitate carries down suspended matter.)
$Al^{3+}(aq) + PO_4^{3-}(aq) \longrightarrow AlPO_4(s)$	Removal of phosphates from wastewater in sewage treatment.
$Mg^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Mg(OH)_2(s)$	Precipitation of magnesium ion from seawater. (First step in the Dow process for extracting magnesium from seawater.)
$Ag^+(aq) + Br^-(aq) \longrightarrow AgBr(s)$	Preparation of AgBr for use in photographic film.
$Zn^{2+}(aq) + SO_4^{2-}(aq) + Ba^{2+}(aq) + S^{2-}(aq) \longrightarrow ZnS(s) + BaSO_4(s)$	Production of *lithopone*, a mixture used as a white pigment in both water paints and oil paints.
$H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow CaHPO_4 \cdot 2\,H_2O(s)$	Preparation of calcium hydrogen phosphate dihydrate, used as a polishing agent in toothpastes.

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Example 4.6

One cup (about 240 g) of a certain clear chicken broth yields 4.302 g AgCl when excess $AgNO_3(aq)$ is added to it. Assuming that all the Cl^- is derived from NaCl, what is the mass of NaCl in the sample of broth?

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4.4 Reactions Involving Oxidation and Reduction

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Reactions Involving Oxidation and Reduction

- ***Oxidation*(氧化反應)**: Loss of electrons
- ***Reduction*(還原反應)**: Gain of electrons
- Both oxidation and reduction must occur simultaneously.
  - A species that loses electrons must lose them ***to*** something else (something that gains them).
  - A species that gains electrons must gain them ***from*** something else (something that loses them).
- Historical: "oxidation" used to mean "combines with oxygen"; the modern definition is much more general.

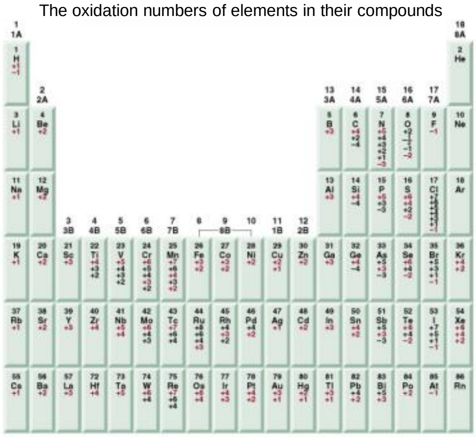
Oxidation Numbers(氧化數)

- An ***oxidation number*** is the charge on an ion, or a *hypothetical* charge assigned to an atom in a molecule or polyatomic ion.
- Examples: in NaCl, the oxidation number of Na is +1, that of Cl is –1 (the actual charge).
- In CO_2 (a molecular compound, no ions) the oxidation number of oxygen is –2, because oxygen as an ion would be expected to have a 2– charge.
- The carbon in CO_2 has an oxidation number of +4 (Why?)

Rules for Assigning Oxidation Numbers

1. *For the atoms in a neutral species—an isolated atom, a molecule, or a formula unit—the sum of all the oxidation numbers is 0.*
2. *For the atoms in an ion, the sum of the oxidation numbers is equal to the charge on the ion.*
3. *In compounds, the group 1A metals all have an oxidation number of +1 and the group 2A metals all have an oxidation number of +2.*
4. *In compounds, the oxidation number of fluorine is –1.*
5. *In compounds, hydrogen has an oxidation number of +1.*
6. *In most compounds, oxygen has an oxidation number of –2.*
7. *In binary compounds with metals, group 7A elements have an oxidation number of –1, group 6A elements have an oxidation number of –2, and group 5A elements have an oxidation number of –3.*

The oxidation numbers of elements in their compounds



Example 4.7

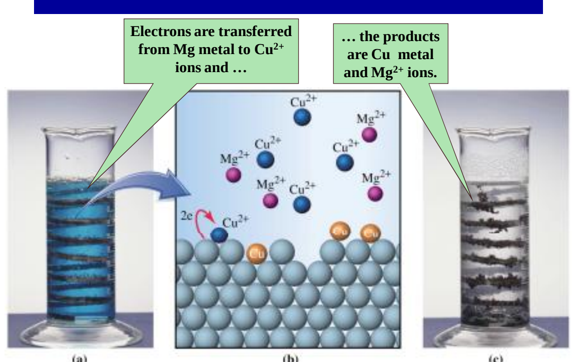
What are the oxidation numbers assigned to the atoms of each element in

(a) $KClO_4$ **(b)** $Cr_2O_7^{2-}$ **(c)** CaH_2 **(d)** Na_2O_2 **(e)** Fe_3O_4

Identifying Oxidation–Reduction Reactions

- In a redox reaction, the oxidation number of a species *changes* during the reaction.
- ***Oxidation*** occurs when the oxidation number increases (species loses electrons).
- ***Reduction*** occurs when the oxidation number decreases (species gains electrons).
- If ***any*** species is oxidized or reduced in a reaction, that reaction is a redox reaction.
- Examples of redox reactions: displacement of an element by another element; combustion; incorporation of an element into a compound, etc.

A Redox Reaction: $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$



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Oxidation–Reduction Equations

- Redox equations must be balanced according to both *mass* and *electric charge*.
- A complete method for balancing such equations will be presented in Chapter 18.
- For now, our main goals will be to:
  - Identify oxidation–reduction reactions.
  - Balance certain simple redox equations by inspection.
  - Recognize, in all cases, whether a redox equation is properly balanced.

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Oxidizing and Reducing Agents

- An ***oxidizing agent*(氧化劑)** causes another substance to be oxidized.
- The oxidizing agent is *reduced*.
- A ***reducing agent*(還原劑)** causes another substance to be reduced.
- The reducing agent is *oxidized*.

$$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$$

What is the oxidizing agent? What is the reducing agent?

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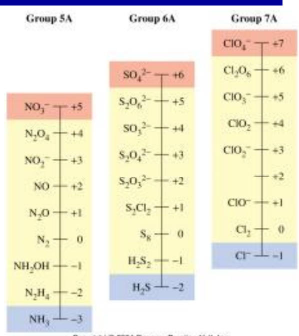
Oxidation Numbers of Nonmetals

- The *maximum* oxidation number of a nonmetal is equal to the *group number*.
  - For nitrogen, +5.
  - For sulfur, +6.
  - For chlorine, +7.
- The *minimum* oxidation number is equal to the (*group number* – 8).



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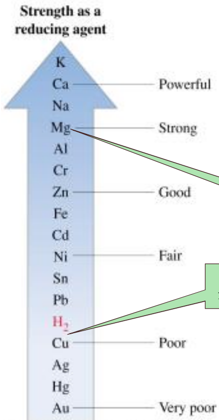
Activity Series of Some Metals



In the activity series, any metal *above* another can displace that other metal.

Mg metal can react with …

… Cu^{2+} ions to form Cu metal.

Will lead metal react with Fe^{3+} ions?

Will iron metal dissolve in an acid to produce H_2 gas?

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Example 4.8 A Conceptual Example

Explain the difference in what happens when a copper-clad penny is immersed in **(a)** hydrochloric acid and **(b)** nitric acid, as shown in Figure 4.14.

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4.5 Applications of Oxidation and Reduction

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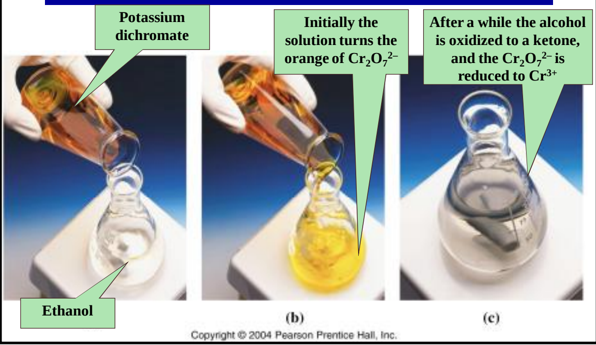
Applications of Oxidation and Reduction

- Everyday life: to clean (bleach) our clothes, sanitize our swimming pools (“chlorine”), and to whiten teeth (peroxide).
- In foods and nutrition: redox reactions “burn” the foods we eat; antioxidants react with undesirable free radicals.
- In industry: to produce iron, steel, other metals, and consumer goods.

Oxidation and Reduction in Organic Chemistry



4.6 Titrations

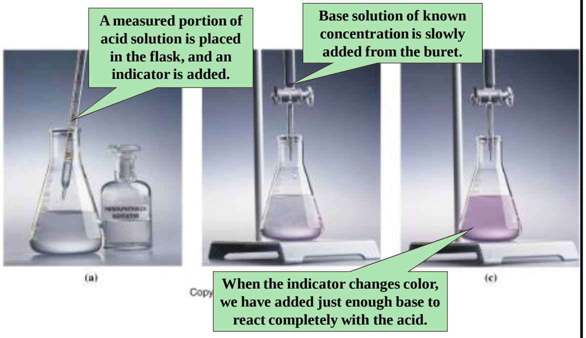
Titrations(滴定)

- In a ***titration***, two reactants in solution are combined carefully until they are in *stoichiometric proportion*.
- The objective of a titration is to determine the number of moles, or the number of grams, or the percentage, or the concentration, of the ***analyte*** (the sought-for substance in an analysis, the substance we are looking for).

Titrations (cont’d)

- In a titration, one reactant (the ***titrant***) is placed in a buret. The other reactant is placed in a flask along with a few drops of an indicator.
- The titrant is slowly added to the contents of the flask until the indicator changes color (the ***endpoint*** 終點).
- If the indicator has been chosen properly, the endpoint tells us when the reactants are present in stoichiometric proportion.
- A titration may be based on any of the previously discussed types of reactions …

An Acid–Base Titration



Titration calculations …

- … are not new to us.
- We simply apply the method of stoichiometry calculations (that we have already done) to the titration.
- Titration calculations for acid–base, precipitation, redox, and other types of titrations are very similar.
- Recall that the objective of a titration is to determine the number of moles, or the number of grams, or the percentage, or the concentration, of the analyte.

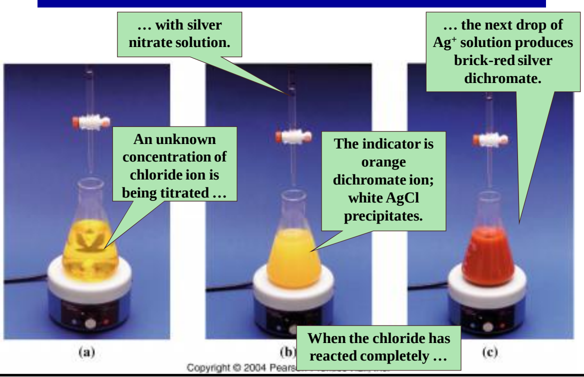
Example 4.9

What volume (mL) of 0.2010 M NaOH is required to neutralize 20.00 mL of 0.1030 M HCl in an acid–base titration?

Example 4.10

A 10.00-mL sample of an aqueous solution of calcium hydroxide is neutralized by 23.30 mL of 0.02000 M HNO_3(aq). What is the molarity of the calcium hydroxide solution?

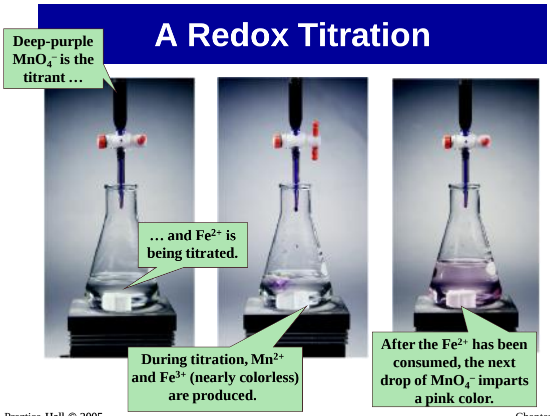
A Precipitation Titration



Example 4.11

Suppose a 0.4096-g sample from a box of commercial table salt is dissolved in water and requires 49.57 mL of 0.1387 M $AgNO_3$(aq) to completely precipitate the chloride ion. If the chloride ion present in solution comes only from the sodium chloride, find the mass of NaCl in the sample. Is commercial table salt pure sodium chloride?

A Redox Titration



Example 4.12

A 0.2865-g sample of an iron ore is dissolved in acid, and the iron is converted entirely to Fe^{2+}(aq). To titrate the resulting solution, 0.02645 L of 0.02250 M $KMnO_4$(aq) is required. What is the mass percent of iron in the ore?