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Chapter 4

Reactions in Aqueous Solution

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Outline

- Precipitation Reactions
- Acid-Base Reactions
- Oxidation-Reduction Reactions

Solubility of Ionic Compounds in Water

- When an ionic compound dissolves in water, two forces compete
 - The attractive forces between the ions in the compound
 - The attractive forces between the water and the ions

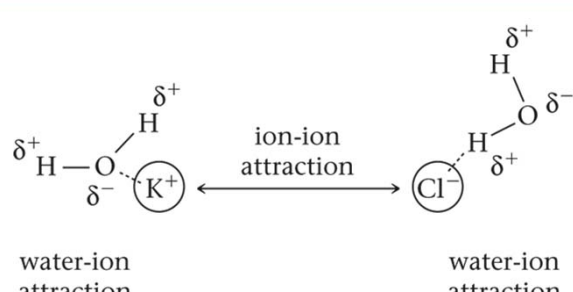
Electrostatic Forces

- If the force of attraction between water molecules and the ions predominates, the compound will be soluble in water
- If the force of attraction between the ions in the compound predominates, the compound will be insoluble in water

Precipitation

- Precipitation in chemical reactions is the formation of a solid where no solid existed before reaction
- Precipitation is the reverse of solubility, where a solid dissolves in a solvent to produce a solution

Figure 4.1: Attractive Forces and Solubility



δ^+ H — O — δ^- (K⁺) \longleftrightarrow (Cl⁻) δ^- — O — H δ^+

water-ion attraction ion-ion attraction water-ion attraction

Will it Dissolve?

- Solubility cannot be determined by first principles
- Solubility can be classified by anion and cation type
 - **Soluble** compounds dissolve in water
 - **Insoluble** compounds do not dissolve

Precipitates

- Precipitates are called **insoluble** – they do not dissolve in solution
- Precipitation of an insoluble solid
 - Mix a solution of nickel(II) chloride with one of sodium hydroxide
 - A solid forms: Ni(OH)_2 (s)

Figure 4.4: Nickel Hydroxide



Figure 4.2 – Precipitation Diagram

	NO_3^-	Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}	PO_4^{3-}
Group 1 cations and NH_4^+						
Group 2 cations			BaSO_4	Mg(OH)_2		
Transition metal cations, Pb^{2+} and Hg_2^{2+}		AgCl^* PbCl_2^* Hg_2Cl_2^*	PbSO_4 Ag_2SO_4			

* The bromides and iodides of these cations are also insoluble.

Solubility Trends

- From the diagram, we see that **some compounds are mostly soluble**
 - Compounds of Group 1 and NH_4^+ cations
 - All nitrates
 - Most chlorides, except for AgCl , PbCl_2 , Hg_2Cl_2
 - Most sulfates, except for BaSO_4 , PbSO_4 , Ag_2SO_4

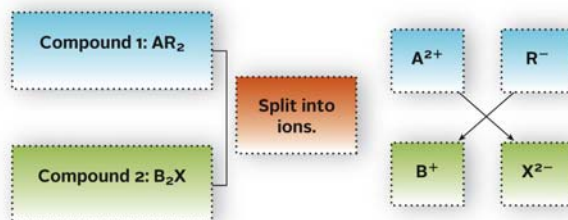
Solubilities Trends

- Some compounds are **mostly insoluble**
 - Carbonates and phosphates, except for the Group I and ammonium
 - Hydroxides, except for the Group 1, Group 2 and ammonium
 - Mg(OH)_2 is insoluble

Working Solubility Problems

- By knowing the rules expressed in Figure 4.2, we can predict what mixtures will precipitate, and what compounds will form

Figure 4.3: Flowchart for Solubility Determination



Example 4.1

EXAMPLE 4.1

Predict what will happen when the following pairs of dilute aqueous solutions are mixed.

- (a) $\text{Cu}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{SO}_4$ (b) FeCl_3 and AgNO_3

STRATEGY

- Follow the schematic diagram in Figure 4.3.
- Use the precipitation diagram (Figure 4.2) to determine whether or not the possible precipitates are soluble.

SOLUTION

(a) Ions in solution	Cu^{2+} and NO_3^- from $\text{Cu}(\text{NO}_3)_2$; NH_4^+ and SO_4^{2-} from $(\text{NH}_4)_2\text{SO}_4$
Possible precipitates	CuSO_4 and NH_4NO_3
Solubility	Both are soluble, no precipitate forms
(b) Ions in solution	Fe^{3+} and Cl^- from FeCl_3 ; Ag^+ and NO_3^- from AgNO_3
Possible precipitates	AgCl and $\text{Fe}(\text{NO}_3)_3$
Solubility	$\text{Fe}(\text{NO}_3)_3$ is soluble, AgCl is insoluble. AgCl precipitates.

Net Ionic Equations

- Consider the precipitation of CaCO_3 from solutions of CaCl_2 and Na_2CO_3
 - Reactants: Ca^{2+} , Cl^- , Na^+ and CO_3^{2-}
 - Products: CaCO_3 , Na^+ and Cl^-
 - Two of the ions are unchanged
 - These are spectator ions
 - Net ionic equation:** leave out the spectator ions
 - $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$

Net Ionic Equations

- Must follow the rules for equations
 - Atoms must balance
 - Charges must balance
 - Show only the ions that react**

Example 4.2

EXAMPLE 4.2

Write a net ionic equation for any precipitation reaction that occurs when dilute solutions of the following ionic compounds are mixed.

- (a) NaOH and $\text{Cu}(\text{NO}_3)_2$ (b) $\text{Ba}(\text{OH})_2$ and MgSO_4 (c) $(\text{NH}_4)_3\text{PO}_4$ and K_2CO_3

STRATEGY

- Follow the plan:
Figure 4.3: compound \rightarrow ions \rightarrow possible precipitates
possible precipitates \rightarrow (Figure 4.2) \rightarrow insoluble compound \rightarrow net ionic equation
- In writing the net ionic equation, start with the insoluble compound on the right, then write the component ions on the left. Do not forget the physical states: ions (aq), product (s).

SOLUTION

(a) Ions in solution	Na^+ and OH^- from NaOH ; Cu^{2+} and NO_3^- from $\text{Cu}(\text{NO}_3)_2$
Possible precipitates	NaNO_3 and $\text{Cu}(\text{OH})_2$
Solubility	NaNO_3 is soluble; $\text{Cu}(\text{OH})_2$ is insoluble.
Net ionic equation	$\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{s})$

continued

Example 4.2, (Cont'd)

SOLUTION	
(b) Ions in solution	Ba ²⁺ and OH ⁻ from Ba(OH) ₂ ; Mg ²⁺ and SO ₄ ²⁻ from MgSO ₄
Possible precipitates	Mg(OH) ₂ and BaSO ₄
Solubility	Both BaSO ₄ and Mg(OH) ₂ are insoluble.
Net ionic equation	$Mg^{2+}(aq) + 2OH^{-}(aq) \rightarrow Mg(OH)_2(s)$ $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$
(c) Ions in solution	NH ₄ ⁺ and PO ₄ ³⁻ from (NH ₄) ₃ PO ₄ ; K ⁺ and CO ₃ ²⁻ from K ₂ CO ₃
Possible precipitates	(NH ₄) ₂ CO ₃ and K ₃ PO ₄
Solubility	Both (NH ₄) ₂ CO ₃ and K ₃ PO ₄ are soluble.
Net ionic equation	no reaction

Why Write Net Ionic Equations?

- Net ionic equations
 - Focus attention on the reaction
 - Simplify calculations
- We will use net ionic equations from now on

Example 4.3

EXAMPLE 4.3 GRADED

When aqueous solutions of sodium hydroxide and iron(III) nitrate are mixed, a red precipitate forms.

- Write a net ionic equation for the reaction.
- What volume of 0.136 M iron(III) nitrate is required to produce 0.886 g of precipitate?
- How many grams of precipitate are formed when 50.00 mL of 0.200 M NaOH and 30.00 mL of 0.125 M Fe(NO₃)₃ are mixed?

ANALYSIS	
Information given:	reactant compounds [NaOH and Fe(NO ₃) ₃]
Asked for:	net ionic equation
STRATEGY	
<ol style="list-style-type: none"> Follow the schematic diagram in Figure 4.3 to determine possible precipitates. Use the precipitation diagram (Figure 4.2) to determine whether the possible precipitates are soluble or insoluble. Write the net ionic equation. Start with the product. 	

continued

Example 4.3, (Cont'd)

SOLUTION	
Ions in solution	Na ⁺ and OH ⁻ from NaOH; Fe ³⁺ and NO ₃ ⁻ from Fe(NO ₃) ₃
Possible precipitates	Fe(OH) ₃ and NaNO ₃
Solubility	Fe(OH) ₃ is insoluble and forms a precipitate.
Net ionic equation	$Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)$
ANALYSIS	
Information given:	net ionic equation from (a): $[Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)]$ mass of precipitate (0.886 g); molarity of Fe(NO ₃) ₃ (0.125 M)
Information implied:	molarity of reacting ion, Fe ³⁺ molar mass of precipitate
Asked for:	volume of Fe(NO ₃) ₃ used in the reaction

continued

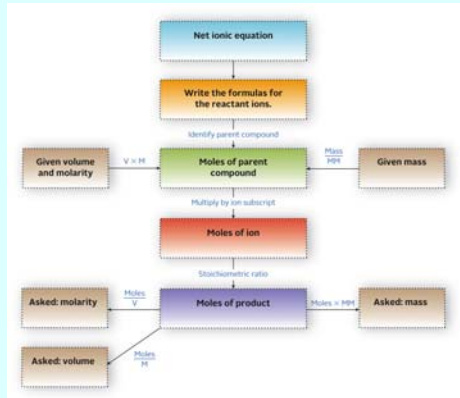
Example 4.3, (Cont'd)

STRATEGY	
Reverse the pathway shown in Figure 4.6. mass Fe(OH) ₃ → mol ppt → mol ion → mol of parent compound → V of parent compound	
SOLUTION	
mol Fe(NO ₃) ₃	$0.886 \text{ g Fe(OH)}_3 \times \frac{1 \text{ mol Fe(OH)}_3}{106.87 \text{ g Fe(OH)}_3} \times \frac{1 \text{ mol Fe}^{3+}}{1 \text{ mol Fe(OH)}_3} \times \frac{1 \text{ mol Fe(NO}_3)_3}{1 \text{ mol Fe}^{3+}} = 0.00829$
V _{Fe(NO₃)₃}	$V = \frac{\text{mol}}{M} = \frac{0.00829 \text{ mol}}{0.125 \text{ mol/L}} = 0.0610 \text{ L}$
ANALYSIS	
Information given:	net ionic equation from (a): $[Fe^{3+}(aq) + 3OH^{-}(aq) \rightarrow Fe(OH)_3(s)]$ volume (50.00 mL) and molarity (0.200 M) of NaOH volume (30.00 mL) and molarity (0.125 M) of Fe(NO ₃) ₃
Information implied:	number of moles of reacting ions, Fe ³⁺ and OH ⁻ Data for moles of both reactants is given, making this a limiting reactant problem.
Asked for:	mass of precipitate formed

Example 4.3, (Cont'd)

STRATEGY	
<ol style="list-style-type: none"> Follow the pathway in Figure 4.6 for both NaOH and Fe(NO₃)₃ to obtain moles of precipitate formed. mol NaOH (V × M) → mol OH⁻ → mol ppt Fe(NO₃)₃(V × M) → mol Fe³⁺ → mol ppt Choose the smaller number of moles and convert moles to mass. 	
SOLUTION	
mol ppt if NaOH limiting	$0.0500 \text{ L} \times 0.200 \frac{\text{mol NaOH}}{\text{L}} \times \frac{1 \text{ mol OH}^{-}}{1 \text{ mol NaOH}} \times \frac{1 \text{ mol Fe(OH)}_3}{3 \text{ mol OH}^{-}} = 0.00333 \text{ mol Fe(OH)}_3$
mol ppt if Fe(NO ₃) ₃ limiting	$0.0300 \text{ L} \times 0.125 \frac{\text{mol Fe(NO}_3)_3}{\text{L}} \times \frac{1 \text{ mol Fe}^{3+}}{1 \text{ mol Fe(NO}_3)_3} \times \frac{1 \text{ mol Fe(OH)}_3}{1 \text{ mol Fe}^{3+}} = 0.00375 \text{ mol Fe(OH)}_3$
Theoretical yield	0.00333 mol < 0.00375 mol; 0.00333 mol Fe(OH) ₃ is obtained
Fe(OH) ₃	$0.00333 \text{ mol} \times \frac{106.87 \text{ g}}{1 \text{ mol}} = 0.356 \text{ g}$

Figure 4.6: Flow Chart for Solution Stoichiometry



Acids and Bases

- Everyday life includes contact with many acids and bases



Strong and Weak Acids and Bases

- Strong acids ionize completely to H^+
 - $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
 - In a solution of 1.0 M HCl, there is 1M H^+ and 1M Cl^-
 - No HCl is left un-ionized
 - Other strong acids ionize in similar fashion

The Double Arrow Notation (\rightleftharpoons)

- Some equations use a double arrow rather than a single arrow
- Note that the double arrow points in both directions
- For now, the double arrow indicates that a reaction does not proceed completely to the right

Weak Acids

- Weak acids ionize only partially
 - $HB(aq) \rightleftharpoons H^+(aq) + B^-(aq)$
 - $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$
- Commonly, weak acids are 5% ionized or less

Strong Bases

- Strong bases ionize completely to OH^-
 - $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$
 - $Ca(OH)_2(s) \rightarrow Ca^{2+}(aq) + 2 OH^-(aq)$

Strong Acids and Bases

TABLE 4.1 Common Strong Acids and Bases

Acid	Name of Acid	Base	Name of Base
HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrobromic acid	NaOH	Sodium hydroxide
HI	Hydriodic acid	KOH	Potassium hydroxide
HNO ₃	Nitric acid	Ca(OH) ₂	Calcium hydroxide
HClO ₄	Perchloric acid	Sr(OH) ₂	Strontium hydroxide
H ₂ SO ₄	Sulfuric acid	Ba(OH) ₂	Barium hydroxide

Weak Bases

- Weak bases react with water to form OH⁻, but the reaction does not go to completion
 - $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
- Commonly, weak bases are 5% ionized or less

Acids and Bases - Reactions

- Acids react with bases
 - Strong acid-strong base
 - Weak acid-strong base
 - Weak base-strong acid

Strong Acid-Strong Base Reaction

- Always the same net ionic equation
 - $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}$
- Note that as usual, net ionic equations use the smallest whole number coefficients
 - $2 \text{HBr}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O} + \text{BaBr}_2(\text{aq})$
 - Still has the same net ionic equation:
 - $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}$

Weak Acid-Strong Base Reaction

- Two steps
 - $\text{HB}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{B}^-(\text{aq})$
 - $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}$
- Overall reaction
 - $\text{HB}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{B}^-(\text{aq}) + \text{H}_2\text{O}$

Weak Base-Strong Acid Reaction

- Two steps
 - $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}$
- Overall reaction
 - $\text{NH}_3(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq})$

Example 4.4

EXAMPLE 4.4

Write a net ionic equation for each of the following reactions in dilute water solution.

- Hypochlorous acid (HClO) and calcium hydroxide.
- Ammonia with perchloric acid (HClO₄).
- Hydriodic acid (HI) with sodium hydroxide.

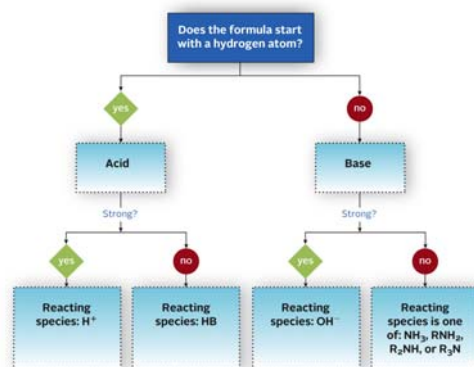
STRATEGY

- Determine the nature of the compound (acid or base; strong or weak) and its reacting species. (Table 4.1 and Figure 4.8 are helpful.)
- Recall Table 4.2 and write a net ionic equation for the acid-base reaction.

SOLUTION

(a) Nature of the compounds reacting species net ionic equation	HClO: weak acid; Ca(OH) ₂ : strong base For HClO: HClO; for Ca(OH) ₂ : OH ⁻ $\text{HClO}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{ClO}^-(\text{aq}) + \text{H}_2\text{O}$
(b) Nature of the compounds reacting species net ionic equation	HClO ₄ : strong acid; NH ₃ : weak base For HClO ₄ : H ⁺ ; for NH ₃ : NH ₃ $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4^+(\text{aq})$
(c) Nature of the compounds reacting species net ionic equation	HI: strong acid; NaOH: strong base For HI: H ⁺ ; for NaOH: OH ⁻ $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}$

Figure 4.8: Flowchart for Acid-Base Reactions



Acid-Base Titrations

- Commonly used to determine the concentration of a dissolved species or its percentage in a mixture
- Titration
 - Measuring the volume of a standard solution (known concentration) needed to react with a measured quantity of a sample

Titration

- Titrant (in the buret)
 - Know concentration
 - Know volume
- Analyte (in the Erlenmeyer flask)
 - Know volume or mass
 - Determine concentration or mass percent by reacting with the titrant

Analyzing for Acetic Acid

- $\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^-(\text{aq}) + \text{H}_2\text{O}$
 - The objective is to determine when the reaction is complete
 - When the number of moles of acid equals the number of moles of OH⁻, the **equivalence point** has been reached
 - Equivalence point is where the number of moles of acid equals the number of moles of base
 - The **endpoint** is indicated by a color change in the acid-base **indicator**

Figure 4.9 – An Acid-Base Titration

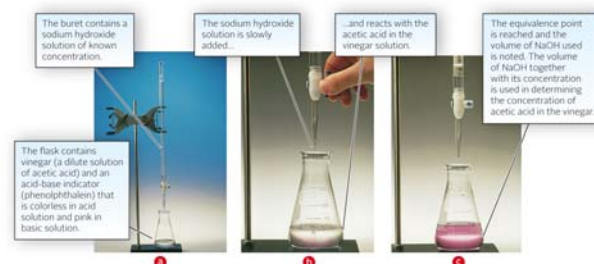
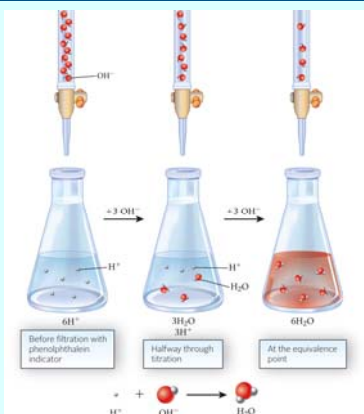


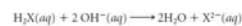
Figure 4.10: Molecular Representation of an Acid-Base Titration



Example 4.5

EXAMPLE 4.5 GRADED

Three beakers labeled A, B, and C contain the weak acid H_2X . The weak acid is titrated with 0.125 M NaOH . Assume the reaction to be



- Beaker A contains 25.00 mL of $0.316\text{ M } H_2X$. What volume of NaOH is required for complete neutralization?
- Beaker B contains 25.00 mL of a solution of H_2X and requires 28.74 mL of NaOH for complete neutralization. What is the molarity of the H_2X solution?
- Beaker C contains 0.124 g of H_2X and 25.00 mL of water. To reach the equivalence point, 22.04 mL of NaOH are required. What is the molar mass of H_2X ? *continued*

Example 4.5, (Cont'd)

ANALYSIS	
Information given:	volume (25.00 mL) and molarity (0.316 M) of H_2X molarity (0.125 M) of NaOH net ionic equation $[H_2X(aq) + 2\text{OH}^-(aq) \rightarrow 2H_2O + X^{2-}(aq)]$
Information implied:	stoichiometric ratio; reacting species
Asked for:	volume of NaOH required for neutralization
STRATEGY	
1. Use the stoichiometric ratio: $2\text{ mol OH}^-/1\text{ mol } H_2X$	
2. Follow the flow chart in Figure 4.6.	
H_2X does not break up into ions. Skip the moles parent compound \rightarrow moles ion step	
$\text{mol } H_2X \xrightarrow{\text{stoichiometric ratio}} \text{mol OH}^- \xrightarrow{\text{mol NaOH}} n + M \rightarrow \text{volume NaOH}$	
SOLUTION	
mol NaOH	$0.02500\text{ L} \times 0.316 \frac{\text{mol } H_2X}{\text{L}} \times \frac{2\text{ mol OH}^-}{1\text{ mol } H_2X} \times \frac{1\text{ mol NaOH}}{1\text{ mol OH}^-} = 0.0158$
Volume of NaOH used	$V = n + M = \frac{0.0158\text{ mol}}{0.125\text{ M}} = 0.126\text{ L}$

Example 4.5, (Cont'd)

ANALYSIS	
Information given:	volume (28.74 mL) and molarity (0.125 M) of NaOH volume of H_2X (25.00 mL) required for complete neutralization net ionic equation $[H_2X(aq) + 2\text{OH}^-(aq) \rightarrow 2H_2O + X^{2-}(aq)]$
Information implied:	stoichiometric ratio
Asked for:	molarity of H_2X
STRATEGY	
1. Use the stoichiometric ratio: $2\text{ mol OH}^-/1\text{ mol } H_2X$	
2. Follow the flow chart in Figure 4.6.	
H_2X does not break up into ions. Skip the moles parent compound \rightarrow moles ion step for H_2X .	
$\text{mol NaOH} \xrightarrow{\text{stoichiometric ratio}} \text{mol OH}^- \xrightarrow{n + V} \text{mol } H_2X \xrightarrow{M_{H_2X}} M_{H_2X}$	
SOLUTION	
Mol H_2X	$0.02874\text{ L} \times 0.125 \frac{\text{mol NaOH}}{\text{L}} \times \frac{1\text{ mol OH}^-}{1\text{ mol NaOH}} \times \frac{1\text{ mol } H_2X}{2\text{ mol OH}^-} = 0.00180$
Molarity of H_2X (M)	$M = n + V = \frac{0.00180\text{ mol}}{0.02500\text{ L}} = 0.0720\text{ M}$

Example 4.5, (Cont'd)

ANALYSIS	
Information given:	volume (22.04 mL) and molarity (0.125 M) of NaOH mass (0.124 g) of H_2X volume (25.00 mL) of water net ionic equation $[H_2X(aq) + 2\text{OH}^-(aq) \rightarrow 2H_2O + X^{2-}(aq)]$
Information implied:	stoichiometric ratio
Asked for:	molar mass of H_2X
STRATEGY	
1. Use the stoichiometric ratio: $2\text{ mol OH}^-/1\text{ mol } H_2X$	
2. Follow the flow chart in Figure 4.6.	
H_2X does not break up into ions. Skip the moles parent compound \rightarrow moles ion step for H_2X .	
$\text{mol NaOH} \xrightarrow{\text{stoichiometric ratio}} \text{mol OH}^- \xrightarrow{m + n} \text{mol } H_2X \xrightarrow{\text{MM of } H_2X} \text{MM of } H_2X$	
SOLUTION	
mol H_2X	$0.02204\text{ L} \times 0.125 \frac{\text{mol NaOH}}{\text{L}} \times \frac{1\text{ mol OH}^-}{1\text{ mol NaOH}} \times \frac{1\text{ mol } H_2X}{2\text{ mol OH}^-} = 0.001378$
molar mass of H_2X	$MM = \frac{m}{n} = \frac{0.124\text{ g}}{0.001378\text{ mol}} = 90.0\text{ g/mol}$
END POINTS	
1. You need to figure out the number of moles before you can calculate mass, molar mass, volume, or molarity.	
2. The amount of water added to the solid H_2X is irrelevant to the solution of the problem.	

Acids and Metals

- Many metals will react with acids, producing hydrogen gas



Oxidation-Reduction Reactions

- Short name: Redox reactions
- Electron exchange
 - Oxidation is a loss of electrons
 - Reduction is a gain of electrons

Rusting of Metal

- When exposed to oxygen, metal containing iron will rust
 - Rust is iron oxide
 - Iron loses electrons
 - Oxygen gains electrons
 - This is a redox reaction



Reaction of Zinc with an Acid

- $\text{Zn (s)} + 2 \text{H}^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + \text{H}_2 \text{(g)}$
- Consider two half equations:
 - Zn loses two electrons
 - $\text{Zn (s)} \rightarrow \text{Zn}^{2+} \text{(aq)} + 2 \text{e}^-$
 - H^+ gains an electron
 - $2\text{H}^+ \text{(aq)} + 2 \text{e}^- \rightarrow \text{H}_2 \text{(g)}$

Redox Principles

- ***Oxidation and reduction must occur together***
- ***There is no net change in the number of electrons in a redox reaction***

Cause and Effect

- Something must cause the zinc to lose two electrons
 - This is the ***oxidizing agent*** – the H^+
- Something must cause the H^+ to gain two electrons
 - This is the ***reducing agent*** – the Zn
- Note that
 - The ***oxidizing agent is reduced***
 - The ***reducing agent is oxidized***
 - Both of these appear as ***reactants*** (not products)

Reducing Agents

- Reducing agents become oxidized
- We know that metals commonly form cations
- ***Metals are generally reducing agents***

Oxidizing Agents

- We know that many nonmetals form anions
- To form an anion, a nonmetal must gain electrons
- **Many nonmetals are good oxidizing agents**

Tracking Electrons – Oxidation Numbers

- As we look at the concept of oxidation numbers it is important to realize that
 - **Oxidation numbers are not real charges**
 - Oxidation numbers **may or may not correspond to ion charges**
 - Oxidation numbers may be fractional

Rules Governing Oxidation Numbers

1. The oxidation number of an element in an **elementary substance** is **zero**.
2. The oxidation number of an **element in a monatomic ion** is the **charge on the ion**
3. Certain elements have the same oxidation number in most compounds
 - a. Group 1 metals are +1
 - b. Group 2 metals are +2
 - c. Oxygen is usually -2
 - d. Hydrogen is usually +1
4. Oxidation numbers sum to zero (compound) or to the charge (polyatomic ion)

Example 4.6

EXAMPLE 4.6

Assign an oxidation number (oxid. no.) to each element in the following species:

- (a) N_2 (b) N^{3-} (c) NO_3^- (d) BaO (e) K_2O_2

continued

Example 4.6 (Cont'd)

SOLUTION

(a) N_2 is in its elementary state. (Rule 1)

oxid. no. N = **0**

(b) N^{3-} is a monoatomic ion. (Rule 2)

oxid. no. N = **-3**

(c) There are no Group 1 or Group 2 metals. (Rule 6)

oxid. no. O = **-2**

NO_3^- is a polyatomic ion. (Rule 5)

$3(-2) + x = -1$; oxid. no. N = **+5**

(d) Ba is a Group 2 metal. (Rule 3)

oxid. no. Ba = **+2**

The sum of the oxidation numbers is 0. (Rule 5)

$+2 + x = 0$; oxid. no. O = **-2**

(e) K is a Group 1 metal. (Rule 3)

oxid. no. K = **+1**

The sum of the oxidation numbers is 0. (Rule 5)

$2(1) + 2x = 0$; oxid. no. O = **-1**

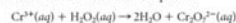
END POINT

Always look for the "leading elements" (Group 1 and Group 2 metals and F) in a compound when you start. These elements will lead you to the oxidation numbers of the other elements in the compound. If these leading elements are not present, then look for H and O (+1 and -2, respectively, when not combined with Group 1 or 2 metals.)

Example 4.7

EXAMPLE 4.7

Consider the unbalanced redox equation:



- (a) Identify the element oxidized and the element reduced.
 (b) What are the oxidizing and reducing agents?

STRATEGY

1. Determine the oxidation number of each element.
2. Find elements whose oxidation numbers change.

SOLUTION

Oxidation numbers

Cr: +3; H: +1; O: -1 → H: +1; O: -2; Cr: +6

Change

Cr: +3 → +6 (increase)

O: -1 → -2 (decrease)

Element reduced

O (decrease in oxidation number)

Element oxidized

Cr (increase in oxidation number)

Oxidizing agent

H_2O_2 (It is the species that contains the element that is reduced.)

Reducing agent

Cr^{3+} (It is the species that contains the element that is oxidized.)

Redox Reactions and Oxidation Numbers

- Oxidation is an increase in oxidation number
 - This is the same as a loss of electrons
- Reduction is a decrease in oxidation number
 - This is the same as a gain of electrons

Balancing Half-Equations (Oxidation or Reduction)

- Balance the atom(s) of the element being oxidized and do the same for the element being reduced.
- Balance the oxidation numbers by adding electrons to the correct side of the half equation.
- Balance charge by adding H^+ (acid) or OH^- (base).
- Balance hydrogens by adding H_2O .
- Check to make sure oxygen is balanced.

Example 4.8

EXAMPLE 4.8

Balance the following half-equations:

- $\text{NO}_3^-(\text{aq}) \rightarrow \text{NO}(\text{g})$ (basic solution)
- $\text{Cl}_2(\text{g}) \rightarrow \text{ClO}_3^-(\text{aq})$ (acidic solution)

STRATEGY

Follow the steps outlined above in the order given.

SOLUTION

- | | |
|------------------------------|--|
| (1) (a) Oxidation numbers | N: $+5 \rightarrow +2$; O: $-2 \rightarrow -2$; N is reduced. |
| (b) Atom balance | 1 N on each side; no adjustment is required. |
| (c) "total oxidation" number | N: $5(1) \rightarrow 2(1)$ |
| (d) Add electrons | The oxidation number for N goes from +5 to +2. It is reduced by 3. Add 3 electrons to the reactant side.
$\text{NO}_3^-(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g})$ |
| (e) Balance charge | reactants: $-1 + 3(-1) = -4$ products: 0
basic medium: add OH^- . To balance, add 4 OH^- on the right.
$\text{NO}_3^-(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 4\text{OH}^-(\text{aq})$
reactants: $-1 + 3(-1) = -4$ products: $4(-1) = -4$ |

continued

Example 4.8, (Cont'd)

SOLUTION

- | | |
|------------------------------|---|
| (f) Balance H | reactants: 0 H products: 4 H
To balance, add $2\text{H}_2\text{O}$ on the left.
$\text{NO}_3^-(\text{aq}) + 3\text{e}^- + 2\text{H}_2\text{O} \rightarrow \text{NO}(\text{g}) + 4\text{OH}^-(\text{aq})$
reactants: 4 H products: 4 H |
| (g) Check O: | reactants: $3 + 2 = 5$ products: $4 + 1 = 5$
The half-equation is balanced:
$\text{NO}_3^-(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 4\text{OH}^-(\text{aq})$ |
| (2) (a) Oxidation numbers | Cl: $0 \rightarrow +5$; O: $-2 \rightarrow -2$; Cl is oxidized. |
| (b) Atom balance | reactant: 2 Cl product: 1 Cl
Multiply ClO_3^- by 2.
$\text{Cl}_2(\text{g}) \rightarrow 2\text{ClO}_3^-(\text{aq})$ |
| (c) "total oxidation" number | Cl: $0(2) = 0 \rightarrow \text{Cl: } 5(2) = 10$ |
| (d) Add electrons | The oxidation number for Cl goes from 0 to 10. The oxidation number increases by 10. Add 10 electrons to the product side.
$\text{Cl}_2(\text{g}) \rightarrow 2\text{ClO}_3^-(\text{aq}) + 10\text{e}^-$ |
| (e) Balance charge | reactants: 0 products: $2(-1) + 10(-1) = -12$
acidic medium: add H^+ . To balance, add 12 H^+ on the right.
$\text{Cl}_2(\text{g}) \rightarrow 2\text{ClO}_3^-(\text{aq}) + 10\text{e}^- + 12\text{H}^+(\text{aq})$
reactants: 0 products: $2(-1) + 10(-1) + 12(+1) = 0$ |
| (f) Balance H | reactants: 0 H products: 12 H
To balance, add $6\text{H}_2\text{O}$ on the left.
$\text{Cl}_2(\text{g}) + 6\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^-(\text{aq}) + 10\text{e}^- + 12\text{H}^+(\text{aq})$
reactants: 12 H products: 12 H |
| (g) Check O: | reactants: 6 products: $2(3) = 6$
The half-equation is balanced:
$\text{Cl}_2(\text{g}) + 6\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^-(\text{aq}) + 10\text{e}^- + 12\text{H}^+(\text{aq})$ |

Balancing Redox Equations

- Split the equation into two half equations.
- Balance one of the half equations.
- Balance the other half equation.
- Combine the two balanced half equations so as to eliminate electrons.

Hint

- In order to split the redox reaction into two half equations, determine the oxidation numbers first
 - One element must be oxidized
 - One element must be reduced

Example 4.9

EXAMPLE 4.9

Balance the following redox reactions.

- $\text{Fe}^{2+}(\text{aq}) + \text{NO}_3^{-}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{NO}(\text{g})$ (basic solution)
- $\text{MnO}_4^{-}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{Mn}^{2+}(\text{aq}) + \text{ClO}_3^{-}(\text{aq})$ (acidic solution)

STRATEGY

Follow the four-step process outlined above in the order given.

Example 4.9, (Cont'd)

SOLUTION

- (1) (a) Split into two half-equations.
- $$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq})$$
- $$\text{NO}_3^{-}(\text{aq}) \rightarrow \text{NO}(\text{g})$$
- (b-c) Balance the half-equations.
- Check the text. This has been done earlier.
- $$\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e^{-}$$
- $$\text{NO}_3^{-}(\text{aq}) + 3e^{-} + 2\text{H}_2\text{O} \rightarrow \text{NO}(\text{g}) + 4\text{OH}^{-}(\text{aq})$$
- (d) Eliminate electrons.
- Multiply the oxidation half-equation by 3.
- $$3[\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + e^{-}]$$
- Combine half-equations.
- $$\text{NO}_3^{-}(\text{aq}) + 3\text{Fe}^{2+}(\text{aq}) + 2\text{H}_2\text{O} \rightarrow \text{NO}(\text{g}) + 4\text{OH}^{-}(\text{aq}) + 3\text{Fe}^{3+}(\text{aq})$$
- (2) (a) Split into two half-equations.
- $$\text{MnO}_4^{-}(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq})$$
- $$\text{Cl}_2(\text{g}) \rightarrow \text{ClO}_3^{-}(\text{aq})$$
- (b-c) Balance the half-equations.
- The oxidation half-equation is balanced in Example 4.8.
- $$\text{Cl}_2(\text{g}) + 6\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^{-}(\text{aq}) + 10e^{-} + 12\text{H}^{+}(\text{aq})$$
- Try to balance the reduction half-equation.
- $$\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5e^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}$$
- (d) Eliminate electrons.
- Multiply the reduction half-equation by 2.
- $$2[\text{MnO}_4^{-}(\text{aq}) + 8\text{H}^{+}(\text{aq}) + 5e^{-} \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}]$$
- Combine half-equations.
- $$\text{Cl}_2(\text{g}) + 6\text{H}_2\text{O} + 2\text{MnO}_4^{-}(\text{aq}) + 16\text{H}^{+}(\text{aq}) \rightarrow 2\text{ClO}_3^{-}(\text{aq}) + 12\text{H}^{+}(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 8\text{H}_2\text{O}$$
- Net ionic equation
- $$6\text{H}_2\text{O} \rightarrow 8\text{H}_2\text{O} = 2\text{H}_2\text{O} \text{ (product side)}$$
- $$16\text{H}^{+} \rightarrow 12\text{H}^{+} = 4\text{H}^{+} \text{ (reactant side)}$$
- Balanced net ionic equation
- $$\text{Cl}_2(\text{g}) + 2\text{MnO}_4^{-}(\text{aq}) + 4\text{H}^{+}(\text{aq}) \rightarrow 2\text{ClO}_3^{-}(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$$

Example 4.9, (Cont'd)

END POINT

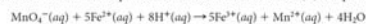
It is a good idea to check both mass and charge balance in the final balanced net ionic equation. In (2), for example:

	Cl Atoms	Mn Atoms	O Atoms	H Atoms	Charge
Left	2	2	2(4) = 8	4	+0 - 2 + 4 = +2
Right	2	2	2(3) + 2 = 8	2(2) = 4	-2 + 4 + 0 = +2

Example 4.10

EXAMPLE 4.10

Consider the balanced equation for the reaction between iron(II) and permanganate ions in acidic solution:



What volume of 0.684 M KMnO_4 solution is required to completely react with 27.50 mL of 0.250 M $\text{Fe}(\text{NO}_3)_2$ (Figure 4.12)?

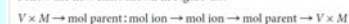
ANALYSIS

Information given:	V (27.50 mL) and M (0.250) of $\text{Fe}(\text{NO}_3)_2$ M (0.684) of KMnO_4
Information implied:	reacting species; stoichiometric ratios
Asked for:	volume of KMnO_4

Example 4.10, (Cont'd)

STRATEGY

Follow the flow chart shown in Figure 4.6.

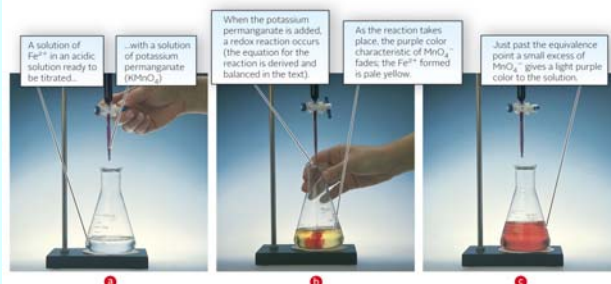


SOLUTION

- Parent \rightarrow ion
 - mol $\text{Fe}(\text{NO}_3)_2$
 - mol Fe^{2+}
 - mol MnO_4^{-}
 - mol KMnO_4
 - V KMnO_4
- $$\text{Fe}(\text{NO}_3)_2 \text{ (parent)} \rightarrow \text{Fe}^{2+} \text{ (ion)}$$
- $$\text{KMnO}_4 \text{ (parent)} \rightarrow \text{MnO}_4^{-} \text{ (ion)}$$
- $$V \times M = (0.02750 \text{ L})(0.250 \text{ mol/L}) = 0.00688$$
- $$0.00688 \text{ mol Fe}(\text{NO}_3)_2 \times \frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Fe}(\text{NO}_3)_2} = 0.00688$$
- $$0.00688 \text{ mol Fe}^{2+} \times \frac{1 \text{ mol MnO}_4^{-}}{5 \text{ mol Fe}^{2+}} = 0.00138$$
- $$0.00138 \text{ mol MnO}_4^{-} \times \frac{1 \text{ mol KMnO}_4}{1 \text{ mol MnO}_4^{-}} = 0.00138$$
- $$\text{moles} = V \times M; V = \frac{0.00138 \text{ mol}}{0.684 \text{ mol/L}} = 0.00202 \text{ L} = \mathbf{2.02 \text{ mL}}$$

Redox Titrations

- Redox reactions can be used to analyze an unknown in the same way as is done with acid-base reactions



Key Concepts – Reactions in Solution



1. Apply the precipitation diagram and schema (Figures 4.2 and 4.3) to
 - Predict solubility and precipitation reactions.
 - Write net ionic equations for precipitation reactions.
2. Perform stoichiometric calculations for reactions.
3. Apply Tables 4.1, 4.2 and Figure 4.8 to write net ionic equations for acid-base reactions.
4. Determine oxidation numbers.
5. Balance half-equations and redox equations.