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Chemistry
Principles and Reactions, 8th Edition
Masterton, Hurley

Chapter 4 Reactions in Aqueous Solution

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Outline

- Solute Concentrations: Molarity
- Precipitation Reactions
- Acid-Base Reactions
- Oxidation-Reduction Reactions

Review

- In Chapter 3, we learned about chemical reactions
 - Most reactions were between pure gases, liquids and solids
 - No solvent was used

Reactions in the Laboratory

- Because water is common everywhere, most chemical reactions take place in aqueous solution
 - Water is called the universal solvent
 - Three common types of reactions in solution:
 - Precipitation reactions
 - Acid-base reactions
 - Oxidation-reduction reactions
- Before we examine each of the three reaction types, we need to examine the concept of molarity

Solute Concentrations - Molarity

- Definition of molarity
 - Molarity = moles of solute/liters of solution
 - Symbol is M
 - Square brackets are used to indicate concentration in M
 - $[\text{Na}^+] = 1.0 \text{ M}$
- Consider a solution prepared from 1.20 mol of substance A, diluted to a total volume of 2.50 L
 - Concentration is 1.20 mol/2.50 L or 0.480 M

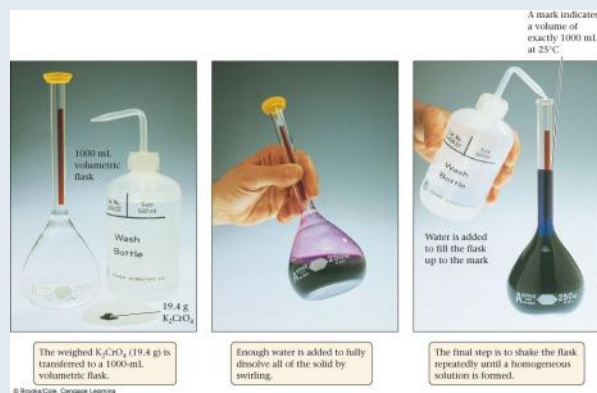
Additivity

- Masses are additive; volumes are not
- The **total mass** of a solution is the **sum of the mass of the solute and the solvent**
- The **total volume** of a solution is **not the sum of the volumes of the solute and solvent**

Volumetric Glassware

- Volumetric pipets, burets and flasks are made so that they contain a known volume of liquid at a given temperature
- Preparing solutions with concentrations in M involves using volumetric glassware

Figure 4.1 – Preparation of Molar Solution



Molarity as a Conversion Factor

- The molarity can be used to calculate
 - The number of moles of solute in a given volume of solution
 - The volume of solution containing a given number of moles of solute

Example 4.1

Example 4.1 Nitric acid, HNO_3 , is extensively used in the manufacture of fertilizer. A bottle containing 75.0 mL of nitric acid solution is labeled 6.0 M HNO_3 .

- How many moles of HNO_3 are in the bottle?
- A reaction needs 5.00 g of HNO_3 . How many mL of solution are required?
- Ten mL of water are added to the solution. What is the molarity of the resulting solution? (Assume volumes are additive.)

Strategy The required conversion factors are

$$\frac{6.0 \text{ mol } HNO_3}{1 \text{ L}} \text{ and } \frac{63.02 \text{ g } HNO_3}{1 \text{ mol}}$$

SOLUTION

$$(a) n_{HNO_3} = 75.0 \text{ mL} \times \frac{6.0 \text{ mol } HNO_3}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.45 \text{ mol}$$

$$(b) V = 5.00 \text{ g} \times \frac{1 \text{ mol } HNO_3}{63.02 \text{ g}} \times \frac{1 \text{ L}}{6.0 \text{ mol } HNO_3} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 13 \text{ mL}$$

(c) From (a) we see that there are 0.45 moles HNO_3 in the solution before addition of the water. That changes the volume (from 75 mL to 85 mL) but not the number of moles. Thus,

$$M = \frac{\text{moles } HNO_3}{V_{\text{solution}}} = \frac{0.45 \text{ moles}}{85.0 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 5.3 \text{ mol/L}$$

Reality Check The molarity decreases when water is added. The moles of solute stay the same, but the volume of the solution increases.

Dissolving Ionic Solids

- When an ionic solid is dissolved in a solvent, the ions separate from each other
 - $MgCl_2(s) \rightarrow Mg^{2+}(aq) + 2Cl^{-}(aq)$
- The concentrations of ions are related to each other by the formula of the compound:
 - Molarity $MgCl_2$ of = molarity of Mg^{2+}
 - Molarity of Cl^{-} = 2 X molarity of $MgCl_2$
 - Total number of moles of ions per mole of $MgCl_2$ is 3

Example 4.2

Example 4.2 Potassium dichromate, $K_2Cr_2O_7$, is used in the tanning of leather. A flask containing 125 mL of solution is labeled 0.145 M $K_2Cr_2O_7$.

- What is the molarity of each ion in solution?
- A sample containing 0.200 moles of K^{+} is added to the solution. Assuming no volume change, what is the molarity of the new solution?

Strategy To go from concentration of solute to concentration of an individual ion, you must know the conversion factor relating moles of ions to moles of solute. To find this conversion factor, it is helpful to write the equation for the solution process.

SOLUTION

(a) $K_2Cr_2O_7(s) \rightarrow 2K^{+}(aq) + Cr_2O_7^{2-}(aq)$.
The conversion factors are 2 mol K^{+} /1 mol $K_2Cr_2O_7$ and 1 mol $Cr_2O_7^{2-}$ /1 mol $K_2Cr_2O_7$. Thus,

$$[K^{+}] = \frac{0.145 \text{ mol } K_2Cr_2O_7}{1 \text{ L}} \times \frac{2 \text{ mol } K^{+}}{1 \text{ mol } K_2Cr_2O_7} = 0.290 \text{ M}$$

$$[Cr_2O_7^{2-}] = \frac{0.145 \text{ mol } K_2Cr_2O_7}{1 \text{ L}} \times \frac{1 \text{ mol } Cr_2O_7^{2-}}{1 \text{ mol } K_2Cr_2O_7} = 0.145 \text{ M}$$

(b) First, find the moles of K^{+} in the original solution:

$$(n_{K^{+}})_{\text{orig}} = \frac{0.290 \text{ mol } K^{+}}{1 \text{ L}} \times 0.125 \text{ L} = 0.03625 \text{ mol}$$

Example 4.2 (cont'd)

Next, we find the molarity of K^+ after the addition of K^+ ions:

$$n_{K^+} = 0.03625 + 0.200 = 0.236$$

$$[K^+] = \frac{0.236 \text{ mol}}{0.125 \text{ L}} = 1.89 \text{ M}$$

Finally, we convert $[K^+]$ to $[K_2Cr_2O_7]$ using the ion-to-solute conversion factor.

$$[K_2Cr_2O_7] = \frac{1.89 \text{ mol } K^+}{1 \text{ L}} \times \frac{1 \text{ mol } K_2Cr_2O_7}{2 \text{ mol } K} = 0.945 \text{ M}$$

Reality Check The concentration of K^+ should be twice that of $Cr_2O_7^{2-}$ in either solution. It is!

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

Will it Dissolve?

- **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



Figure 4.3 – Precipitation Diagram

	NO_3^-	Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}	PO_4^{3-}
Group 1 cations (Na^+ , K^+) and NH_4^+						
Group 2 cations (Mg^{2+} , Ca^{2+} , Ba^{2+})			$BaSO_4$	$Mg(OH)_2$		
Transition metal cations (Figure 4.2)		$AgCl$				

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Solubility Trends

- From the diagram, we see that **some compounds are mostly soluble**
 - Compounds of Group 1 and NH_4^+ cations
 - All nitrates
 - All chlorides, except for AgCl
 - All sulfates, except for BaSO_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 Figure 4.3, we can predict what mixtures will precipitate, and what compounds will form

Example 4.3

Example 4.3 Using the precipitation diagram (Figure 4.3), predict what will happen when the following pairs of aqueous solutions are mixed.

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

Strategy First decide what cation and anion are present in each solution. Then write the formulas of the two possible precipitates, combining a cation of one solution with the anion of the other solution. Check Figure 4.3 to see if one or both of these compounds are insoluble. If so, a precipitation reaction occurs.

Example 4.3 (cont'd)

SOLUTION

(a) Ions present in the first solution: Cu^{2+} , NO_3^- ; the second solution: NH_4^+ , SO_4^{2-}
Possible precipitates: CuSO_4 , NH_4NO_3

From Figure 4.3, both of these compounds are soluble, so **no precipitate forms.**

(b) Ions present: Fe^{3+} , Cl^- ; Ag^+ , NO_3^-

Possible precipitates: AgCl , $\text{Fe(NO}_3)_3$

Iron(III) nitrate is soluble, but silver chloride is not. When these two solutions are mixed, **silver chloride 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 4.4

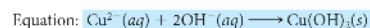
Example 4.4 Write a net ionic equation for any precipitation reaction that occurs when solutions of the following ionic compounds are mixed.

- (a) NaOH and Cu(NO₃)₂ (b) BaCl₂ and Ag₂SO₄ (c) (NH₄)₃PO₄ and K₂CO₃

Strategy Follow the procedure of Example 4.3 to decide whether a precipitate will form. If it does, write its formula, followed by (s), on the right side of the equation. On the left (reactant) side, write the formulas of the ions (aq) required to produce the precipitate. Finally, balance the equation.

SOLUTION

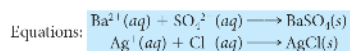
(a) Ions present: Na⁺, OH⁻; Cu²⁺, NO₃⁻
Possible precipitates: NaNO₃, Cu(OH)₂
NaNO₃ is soluble, but Cu(OH)₂ is not.



Example 4.4 (cont'd)

(b) Ions present: Ba²⁺, Cl⁻; Ag⁺, SO₄²⁻
Possible precipitates: BaSO₄, AgCl

Both compounds are insoluble, so two reactions occur.



(c) Ions present: NH₄⁺, PO₄³⁻; K⁺, CO₃²⁻

Both possible products are soluble, so there is **no precipitation reaction** and no equation.

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 4.5 - Precipitation Stoichiometry

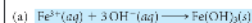
Example 4.5 Graded

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

- * (a) Write a net ionic equation for the reaction.
- ** (b) What volume of 0.136 M iron(III) nitrate is required to produce 0.886 g of precipitate?
- *** (c) 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?

Example 4.5 - Precipitation Stoichiometry

SOLUTION



(b) Determine the number of moles of precipitate. The molar mass of Fe(OH)₃ is 106.87 g/mol, so

$$n_{\text{Fe}(\text{OH})_3} = 0.886 \text{ g} \times \frac{1 \text{ mol}}{106.87 \text{ g}} = 8.29 \times 10^{-3} \text{ mol}$$

Note that in the reaction, one mole of Fe³⁺ produces one mole of Fe(OH)₃. Thus,

$$n_{\text{Fe}^{3+}} = 8.29 \times 10^{-3} \text{ mol}$$

You will need the molarity of Fe(NO₃)₃ to determine the volume required. Since there is one ion of Fe³⁺ in Fe(NO₃)₃,

$$n_{\text{Fe}(\text{NO}_3)_3} = 8.29 \times 10^{-3} \text{ mol}$$

To determine the volume, use the relation $n = V \times M$:

$$V = \frac{8.29 \times 10^{-3} \text{ mol}}{0.136 \text{ mol/L}} = 0.0610 \text{ L}$$

(c) This is a limiting-reactant problem. Specific amounts of both reactants are given. First, find the moles of Fe(OH)₃ produced if Fe³⁺ is limiting.

$$n_{\text{Fe}(\text{OH})_3} = \frac{0.0300 \text{ L} \times 0.125 \text{ mol Fe}(\text{NO}_3)_3}{1 \text{ L}} \times \frac{1 \text{ mol Fe}^{3+}}{1 \text{ mol Fe}(\text{NO}_3)_3} \times \frac{1 \text{ mol Fe}(\text{OH})_3}{1 \text{ mol Fe}^{3+}} = 0.00375 \text{ mol}$$

Example 4.5 - Precipitation Stoichiometry

If OH^- is limiting,

$$n_{\text{Fe}(\text{OH})_3} = \frac{0.0500 \text{ L} \times 0.200 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} \times \frac{1 \text{ mol Fe}(\text{OH})_3}{3 \text{ mol OH}^-} = 0.00333 \text{ mol}$$

Because 0.00333 is less than 0.00375, OH^- is the limiting reactant. The theoretical yield of $\text{Fe}(\text{OH})_3$ is 0.00333 mol. So, the mass produced is

$$0.00333 \text{ mol Fe}(\text{OH})_3 \times \frac{106.87 \text{ g Fe}(\text{OH})_3}{1 \text{ mol Fe}(\text{OH})_3} = 0.356 \text{ g Fe}(\text{OH})_3$$

Acids and Bases

- Everyday life includes contact with many acids and bases



Strong and Weak Acids and Bases

- Strong acids ionize completely to H^+
 - $\text{HCl}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
 - 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
 - $\text{HB}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{B}^-(\text{aq})$
 - $\text{HF}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$
- Commonly, weak acids are 5% ionized or less

Strong Bases

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

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	Hydroiodic 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

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Weak Bases

- Weak bases ionize only partially
 - $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - $\text{CH}_3\text{NH}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
- 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
 - $2 \text{HBr}(\text{aq}) + \text{Ba}(\text{OH})_2(\text{aq}) \rightarrow 2 \text{H}_2\text{O} + \text{CaBr}_2(\text{aq})$
 - 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 4.6

Example 4.6 Write a net ionic equation for each of the following reactions in dilute water solution.

- (a) Hypochlorous acid (HClO) and calcium hydroxide.
- (b) Ammonia with perchloric acid (HClO₄).
- (c) Hydroiodic acid (HI) with sodium hydroxide.

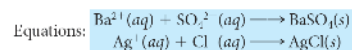
Strategy Decide whether the acid and base are strong or weak. Then decide which of the three types of acid-base reactions is involved. Finally, use Table 4.2 to derive the proper equation.

Example 4.6 (cont'd)

(b) Ions present: Ba²⁺, Cl⁻; Ag⁺, SO₄²⁻

Possible precipitates: BaSO₄, AgCl

Both compounds are insoluble, so two reactions occur.



(c) Ions present: NH₄⁺, PO₄³⁻, K⁺, CO₃²⁻

Both possible products are soluble, so there is **no precipitation reaction** and no equation.

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

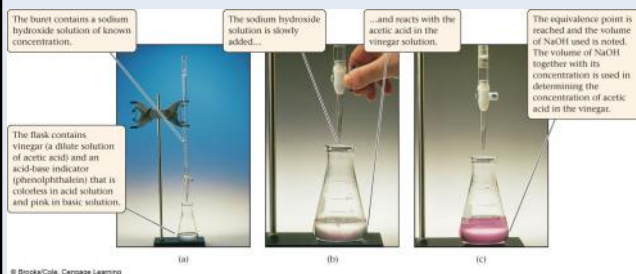
Titration

- 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**

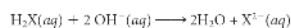
Figure 4.7 – An Acid-Base Titration



Example 4.7

Example 4.7 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



- * (a) Beaker A contains 25.00 mL of $0.316\text{ M } H_2X$. What volume of $NaOH$ is required for complete neutralization?
- ** (b) 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?
- *** (c) 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 ?

Strategy Use the conversion factor obtained from the equation for the reaction:



Also, remember

$$n = V \times M \quad \text{and} \quad n = \frac{m}{MM}$$

Example 4.7 (cont'd)

SOLUTION

(a) Start by using data on H_2X . That will give you the moles of H_2X .

$$n_{H_2X} = 0.02500\text{ L} \times \frac{0.316\text{ mol } H_2X}{1\text{ L}} = 7.90 \times 10^{-3}\text{ mol}$$

$$n_{OH^-} = 2.00 \times 10^{-2}\text{ mol } H_2X \times \frac{2\text{ mol } OH^-}{1\text{ mol } H_2X} = 0.0158\text{ mol}$$

$$V_{NaOH} = \frac{n_{OH^-}}{M_{NaOH}} = \frac{0.0158\text{ mol}}{0.125\text{ mol/L}} = 0.126\text{ L}$$

(b) This time you have all the data (V and M) to determine the moles of OH^- .

$$n_{OH^-} = 0.02874\text{ L} \times \frac{0.125\text{ mol } OH^-}{1\text{ L}} = 3.59 \times 10^{-3}\text{ mol}$$

$$n_{H_2X} = 1.79 \times 10^{-3}\text{ mol } OH^- \times \frac{1\text{ mol } H_2X}{2\text{ mol } OH^-} = 8.95 \times 10^{-4}\text{ mol}$$

$$M_{H_2X} = \frac{n_{H_2X}}{V_{H_2X}} = \frac{8.95 \times 10^{-4}\text{ mol}}{0.02500\text{ L}} = 0.0358\text{ M}$$

(c) We start by finding n_{OH^-} .

$$n_{OH^-} = 0.02204\text{ L} \times \frac{0.125\text{ mol } OH^-}{1\text{ L}} = 2.75 \times 10^{-3}\text{ mol}$$

$$n_{H_2X} = 1.375 \times 10^{-3}\text{ mol } OH^- \times \frac{1\text{ mol } H_2X}{2\text{ mol } OH^-} = 6.875 \times 10^{-4}\text{ mol}$$

$$MM_{H_2X} = \frac{m_{H_2X}}{n_{H_2X}} = \frac{0.124\text{ g}}{6.875 \times 10^{-4}\text{ mol}} = 180.2\text{ g/mol}$$

Reality Check In part (c), note that 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

Reaction of Zinc with an Acid

- $Zn(s) + 2 H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$
- Consider two half equations:
 - Zn loses two electrons
 - $Zn(s) \longrightarrow Zn^{2+}(aq) + 2 e^-$
 - H^+ gains an electron
 - $2 H^+(aq) + 2 e^- \longrightarrow H_2(g)$

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 a **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 4.8

Example 4.8 What is the oxidation number of phosphorus in sodium phosphite, Na_3PO_3 ? In the dihydrogen phosphate ion?

Strategy First look for elements whose oxidation number is always or almost always the same (rule 3). Then solve for the oxidation number of phosphorus, applying rule 4.

SOLUTION In Na_3PO_3 , the oxidation numbers of Na and O are +1 and -2, respectively. Since this compound, like all others, is neutral, the sum of the oxidation numbers must be zero. Letting x be the oxidation number of phosphorus then,

$$0 = 3(+1) + x + 3(-2) \quad x = \text{oxidation number of P} = +3$$

In the $H_2PO_4^-$ ion, hydrogen and oxygen have oxidation numbers of +1 and -2, respectively. The ion has a charge of -1, so the sum of the oxidation numbers must be -1 (rule 4). Letting y be the oxidation number of phosphorus,

$$-1 = y - 2(+1) + 4(-2) \quad y = \text{oxidation number of P} = +5$$

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)

- A. Balance the atom of the element being oxidized or reduced.
- B. Balance the oxidation numbers by adding electrons
- C. Balance charge by adding H^+ (acid) or OH^- (base).
- D. Balance hydrogens by adding H_2O .
- E. Check to make sure oxygen is balanced.

Example 4.9

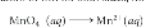
Example 4.9 Balance the following half-equations:

- (1) $\text{MnO}_4^- (\text{aq}) \longrightarrow \text{Mn}^{2+} (\text{aq})$ (acidic solution)
(2) $\text{Cr}(\text{OH})_3 (\text{s}) \longrightarrow \text{CrO}_4^{2-} (\text{aq})$ (basic solution)

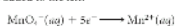
Strategy Follow the rules outlined above, step by step in the proper order, and see what happens.

SOLUTION

(1) (a) Because there is one atom of Mn on both sides, no adjustment is required.



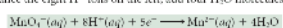
(b) Because manganese is reduced from an oxidation number of +7 to +2, five electrons must be added to the left.



(c) There is a total charge of -6 on the left versus +2 on the right. To balance, add eight H^+ to the left to give a charge of +2 on both sides.



(d) To balance the eight H^+ ions on the left, add four H_2O molecules to the right.



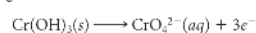
(e) Note that there are the same number of oxygen atoms, four, on both sides, as there should be. The equation shown in green is the correctly balanced reduction half-equation.

Example 4.9 (cont'd)

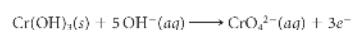
(2) (a) Again, there is one chromium atom on both sides.



(b) Because the oxidation number of chromium increases from +3 to +6, add three electrons to the right.



(c) There is a charge of zero on the left, -5 on the right. To balance charge, add five OH^- ions to the left.



(d) There are eight hydrogens on the left, none on the right. Add four H_2O molecules to the right.



(e) There are eight oxygen atoms on both sides; the oxidation half-equation is properly balanced.

Balancing Redox Equations

1. Split the equation into two half equations.
2. Balance one of the half equations.
3. Balance the other half equation.
4. 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 4.10

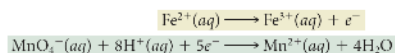
Example 4.10 Balance the following redox equations.

- (a) $\text{Fe}^{2+}(aq) + \text{MnO}_4^{-}(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{Mn}^{2+}(aq)$ (acidic solution)
 (b) $\text{Cl}_2(g) + \text{Cr}(\text{OH})_3(s) \longrightarrow \text{Cl}^{-}(aq) + \text{CrO}_4^{2-}(aq)$ (basic solution)

Strategy Follow the four-step procedure described above. Actually, if you look carefully at the text preceding this example, you'll find that all the half-equations have already been balanced! The color coding should help you find them.

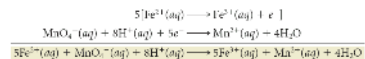
SOLUTION

- (a) (1) oxidation: $\text{Fe}^{2+}(aq) \longrightarrow \text{Fe}^{3+}(aq)$
 reduction: $\text{MnO}_4^{-}(aq) \longrightarrow \text{Mn}^{2+}(aq)$
 (2), (3) The balanced half-equations, as obtained previously, are

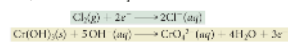


Example 4.10 (cont'd)

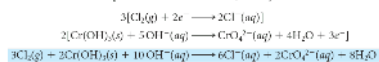
- (4) To eliminate electrons, multiply the oxidation half-equation by 5 and add to the reduction half-equation.



- (b) (1) reduction: $\text{Cl}_2(g) \longrightarrow \text{Cl}^{-}(aq)$
 oxidation: $\text{Cr}(\text{OH})_3(s) \longrightarrow \text{CrO}_4^{2-}(aq)$
 (2), (3) Earlier, the balanced half-equations were found to be



- (4) Multiply the reduction half-equation by 3, the oxidation half-equation by 2, then add. This will produce $6e^{-}$ on both sides, so they will cancel.

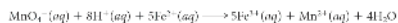


Reality Check It's a good idea to check mass and charge balance in the final equation. In part (b), for example,

	Cl Atoms	Cr Atoms	O Atoms	H Atoms	Charge
Left	6	2	16	16	-10
Right	6	2	16	16	-10

Example 4.11

Example 4.11 As you found in Example 4.10, the balanced equation for the reaction between KMnO_4 and Fe^{2+} in acidic solution is



What volume of 0.684 M KMnO_4 solution is required to react completely with 27.50 mL of 0.250 M $\text{Fe}(\text{NO}_3)_2$ (Figure 4.9, p. 92)?

Strategy (1) Start by calculating the number of moles of Fe^{2+} . Then (2) use the coefficients of the balanced equation to find the number of moles of MnO_4^{-} . Finally, (3), use molarity as a conversion factor to find the volume of KMnO_4 solution.

SOLUTION

$$(1) n_{\text{Fe}^{2+}} = 0.02750 \text{ L} \times \frac{0.250 \text{ mol Fe}(\text{NO}_3)_2}{1 \text{ L}} \times \frac{1 \text{ mol Fe}^{2+}}{1 \text{ mol Fe}(\text{NO}_3)_2}$$

$$= 6.88 \times 10^{-3} \text{ mol Fe}^{2+}$$

$$(2) n_{\text{MnO}_4^{-}} = 0.06888 \text{ mol Fe}^{2+} \times \frac{1 \text{ mol MnO}_4^{-}}{5 \text{ mol Fe}^{2+}} = 0.0138 \text{ mol MnO}_4^{-}$$

$$(3) n_{\text{KMnO}_4} = n_{\text{MnO}_4^{-}} = 1.38 \times 10^{-3} \text{ mol KMnO}_4$$

$$V = 1.38 \times 10^{-3} \text{ mol KMnO}_4 \times \frac{1 \text{ L}}{0.684 \text{ mol KMnO}_4} = 2.02 \times 10^{-3} \text{ L (2.02 mL)}$$

Redox Titrations

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

(a) A solution of Fe^{2+} in an acidic solution ready to be titrated...

(b) ...with solution of potassium permanganate (KMnO_4)

When the potassium permanganate is added, a redox reaction occurs (the equation for the reaction is derived and balanced in the text).

As the reaction takes place, the purple color characteristic of MnO_4^{-} fades; the Fe^{3+} formed is pale yellow.

(c) Just past the equivalence point, a small excess of MnO_4^{-} gives a light purple color to the solution.

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Key Concepts – Reactions in Solution

- Relate molarity to moles and volume.
- Apply the precipitation diagram.
- Carry out stoichiometric calculations for reactions in solution
- Use tables 4.1 and 4.2 to write net-ionic acid-base reactions.
- Determine oxidation numbers.
- Balance half-equations and redox equations.