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Chapter 4

Reactions in Aqueous Solutions

Solutions

A ***solution*** is a homogenous mixture of 2 or more substances.

The ***solute*** is (are) the substance(s) present in the smaller amount(s).

The ***solvent*** is the substance present in the larger amount.

Solution	**Solvent**	**Solute**
Soft drink (*l*)	H_2O	Sugar, CO_2
Air (*g*)	N_2	O_2, Ar, CH_4
Soft solder (*s*)	Pb	Sn

aqueous solutions of $KMnO_4$

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Electrolytes 1

An ***electrolyte*** is a substance that, when dissolved in water, results in a solution that can conduct electricity.

A ***nonelectrolyte*** is a substance that, when dissolved, results in a solution that does not conduct electricity.

$C_6H_{12}O_6$

nonelectrolyte

CH_3COOH

weak electrolyte

NaCl

strong electrolyte

(Left, middle, right images): Stephen Frisch/McGraw Hill

Electrolytes 2

Conduct electricity in solution?

Cations **(+)** and Anions (−)

Strong Electrolyte – **100% dissociation**

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

Weak Electrolyte – **not completely dissociated**

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

Electrolytes 3

Ionization of acetic acid

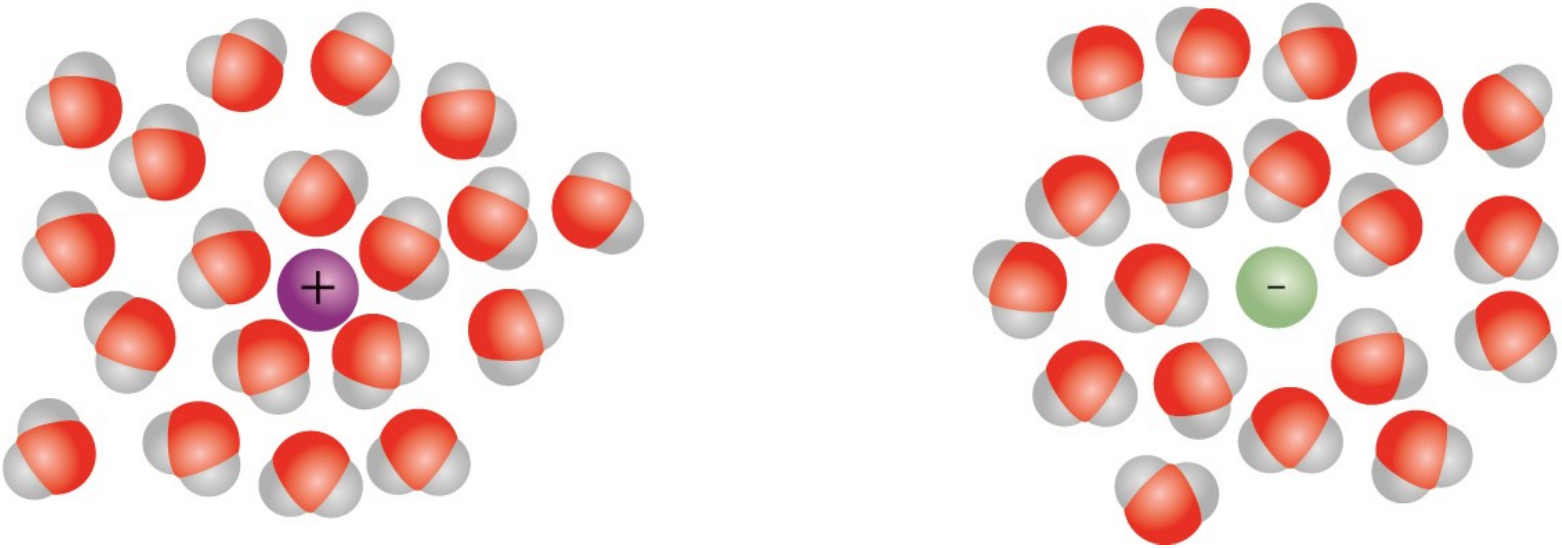
$$\mathrm{CH_3COOH}(aq) \square \mathrm{CH_3COO^-}(aq) + \mathrm{H^+}(aq)$$

⇄ A ***reversible*** reaction. The reaction can occur in both directions.

Acetic acid is a ***weak electrolyte*** because its ionization in water is incomplete.

Hydration

Hydration is the process in which an ion is surrounded by water molecules arranged in a specific manner.



Electrolytes 4

Nonelectrolyte does not conduct electricity

No cations **(+)** and anions (−) in solution

$$C_6H_{12}O_6(s) \xrightarrow{H_2O} C_6H_{12}O_6(aq)$$

Table 4.1 Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HNO_3	HF	CH_3OH (methanol)
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
H_2SO_4*	NH_3	$C_6H_{12}O_6$ (glucose)
NaOH	H_2O†	$C_{12}H_{22}O_{11}$ (sucrose)
$Ba(OH)_2$		
Ionic compounds		

*H_2SO_4 has two ionizable H^+ ions, but only one of the H^+ ions is totally ionized.

†Pure water is an extremely weak electrolyte.

Precipitation Reactions

Precipitation reaction, which results in the formation of an insoluble product, known as a **precipitate**.
Precipitate: insoluble solid that separates from solution.

molecular equation:

$$Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow \overset{\substack{\text{precipitate}\\ \downarrow}}{PbI_2}\ (s) + 2NaNO_3(aq)$$

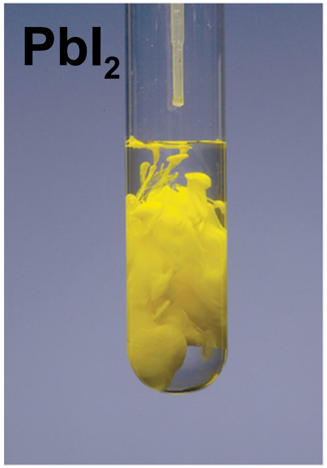
ionic equation:

$$Pb^{2+}(aq) + \cancel{2NO_3^-(aq)} + \cancel{2Na^+(aq)} + 2I^-(aq) \rightarrow PbI_2(s) + \cancel{2Na^+(aq)} + \cancel{2NO_3^-(aq)}$$

net ionic equation:

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

Na^+ and NO_3^- are ***spectator*** ions



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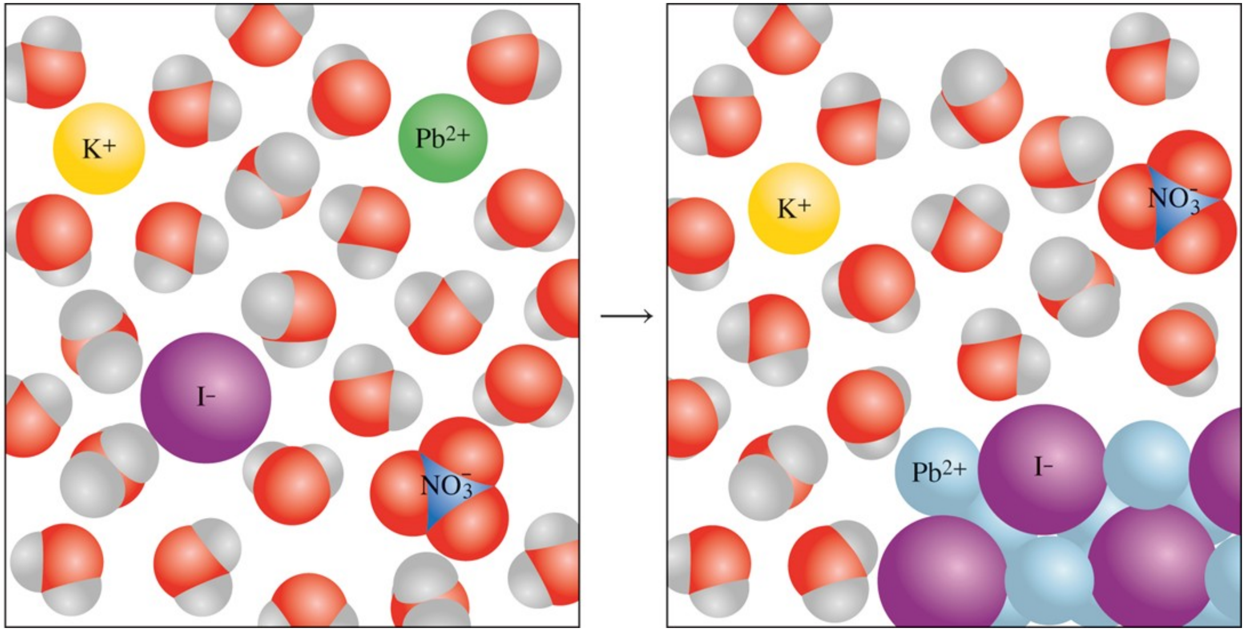
Precipitation of Lead Iodide



$$Pb^{2+}(aq) + 2I^{-}(aq) \rightarrow PbI_2(s)$$

PbI_2

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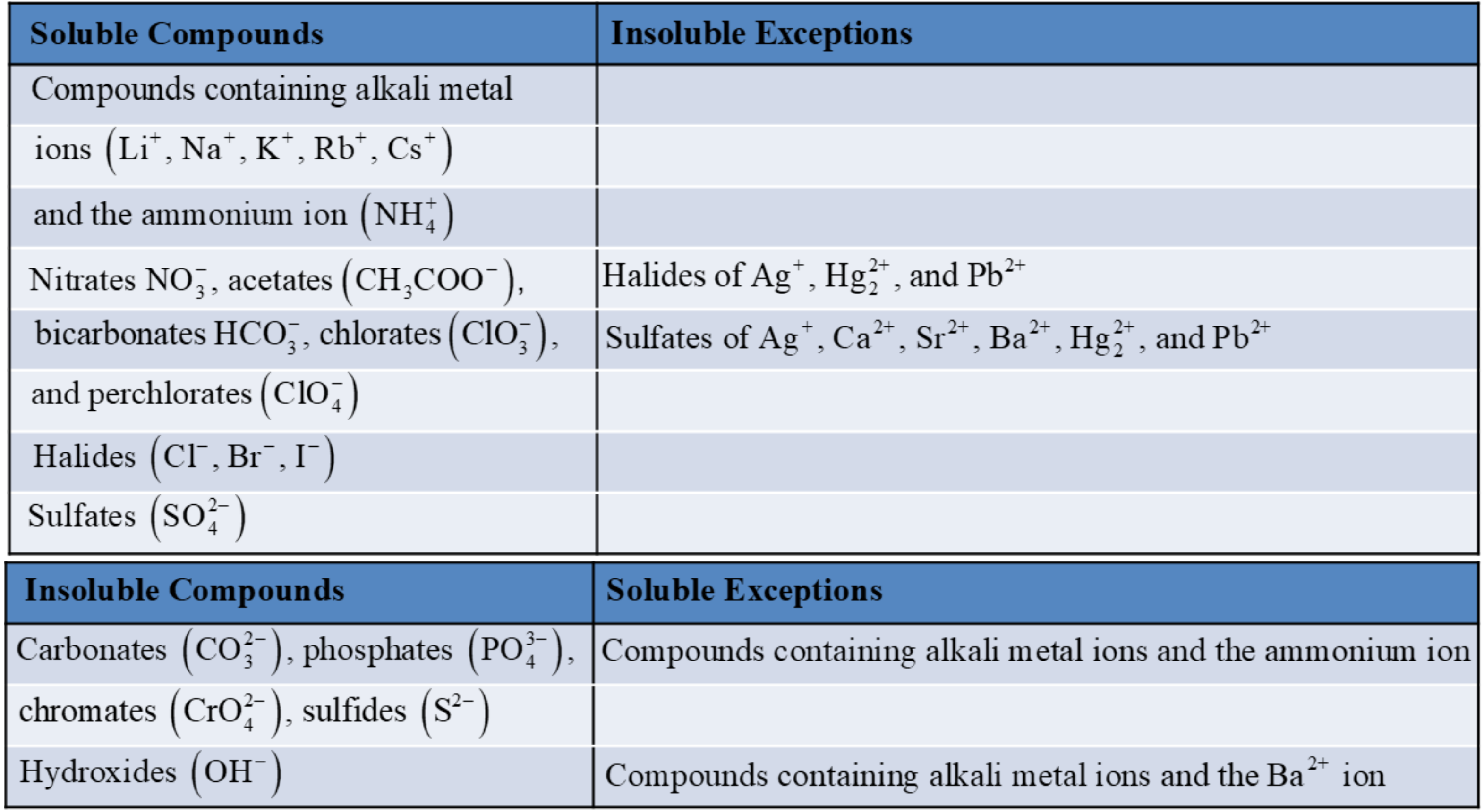
Solubility

Solubility is the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.

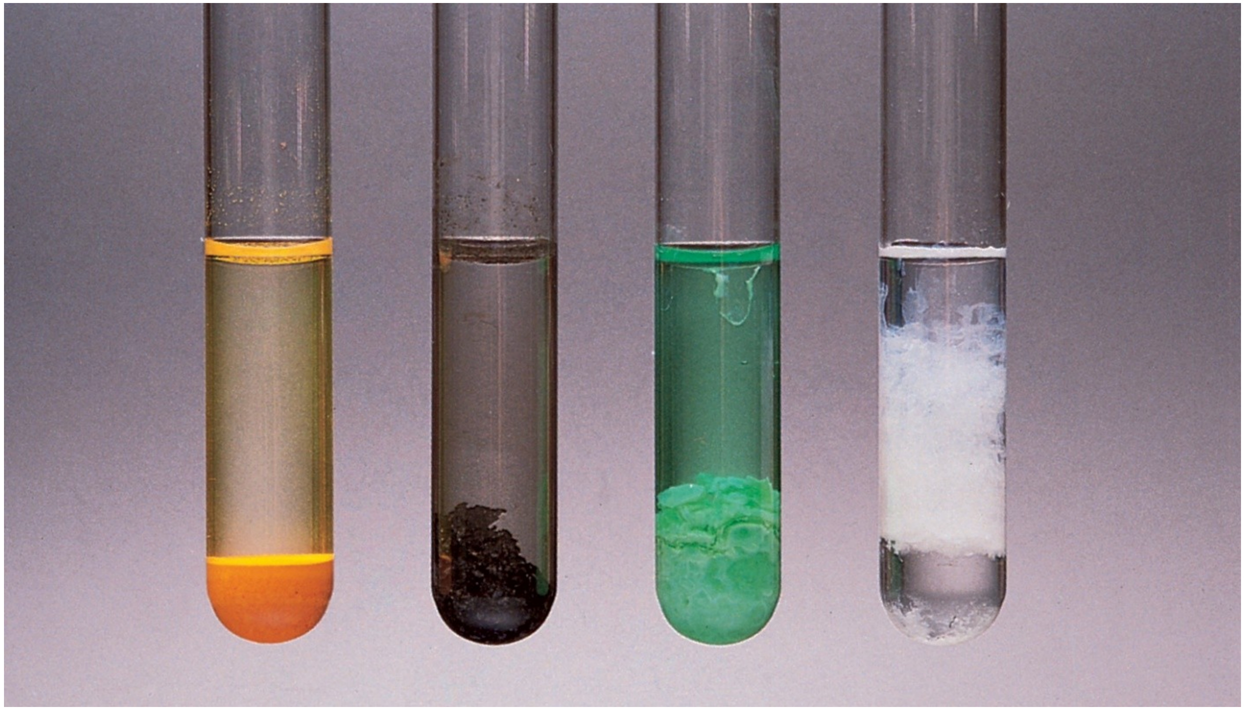
Table 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C



Soluble Compounds	**Insoluble Exceptions**
Compounds containing alkali metal	
ions $(Li^+, Na^+, K^+, Rb^+, Cs^+)$	
and the ammonium ion (NH_4^+)	
Nitrates NO_3^-, acetates (CH_3COO^-),	Halides of Ag^+, Hg_2^{2+}, and Pb^{2+}
bicarbonates HCO_3^-, chlorates (ClO_3^-),	Sulfates of Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}
and perchlorates (ClO_4^-)	
Halides (Cl^-, Br^-, I^-)	
Sulfates (SO_4^{2-})	

Insoluble Compounds	**Soluble Exceptions**
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}),	Compounds containing alkali metal ions and the ammonium ion
chromates (CrO_4^{2-}), sulfides (S^{2-})	
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Examples of Insoluble Compounds



CdS Pbs $Ni(OH)_2$ $Al(OH)_3$

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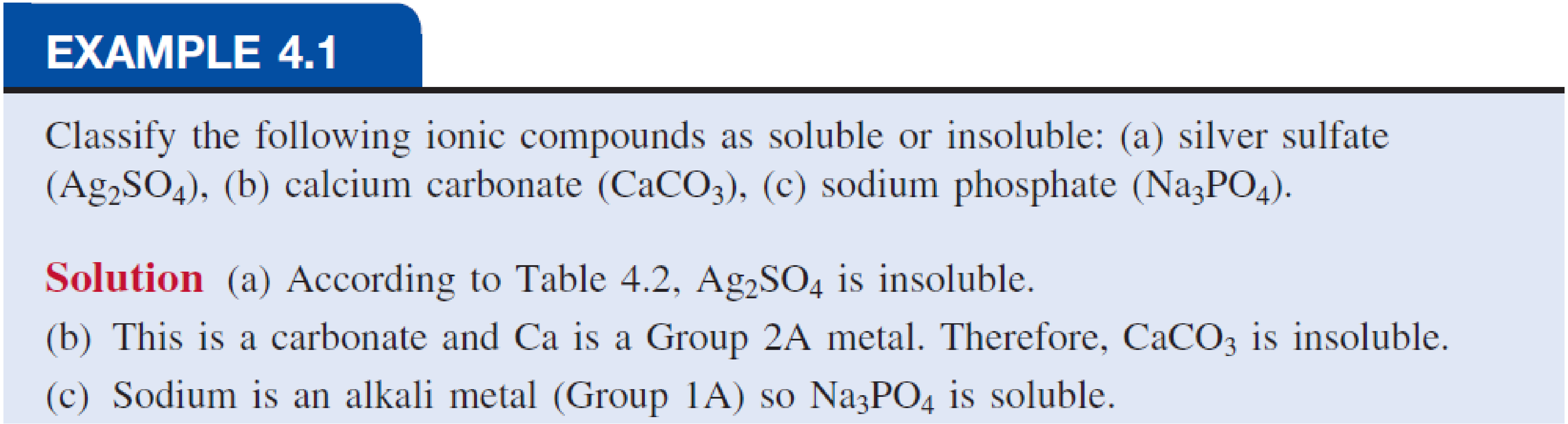
Writing Net Ionic Equations

1. Write the balanced molecular equation.
2. Write the ionic equation showing the strong electrolytes completely dissociated into cations and anions.
3. Cancel the spectator ions on both sides of the ionic equation.
4. Check that charges and number of atoms are balanced in the net ionic **equation**.



EXAMPLE 4.1

Classify the following ionic compounds as soluble or insoluble: (a) silver sulfate (Ag_2SO_4), (b) calcium carbonate ($CaCO_3$), (c) sodium phosphate (Na_3PO_4).

Solution (a) According to Table 4.2, Ag_2SO_4 is insoluble.

(b) This is a carbonate and Ca is a Group 2A metal. Therefore, $CaCO_3$ is insoluble.

(c) Sodium is an alkali metal (Group 1A) so Na_3PO_4 is soluble.

EXAMPLE 4.2

Predict what happens when a potassium phosphate (K_3PO_4) solution is mixed with a calcium nitrate [$Ca(NO_3)_2$] solution. Write a net ionic equation for the reaction.

Solution In solution, K_3PO_4 dissociates into K^+ and PO_4^{3-} ions and $Ca(NO_3)_2$ dissociates into Ca^{2+} and NO_3^- ions. According to Table 4.2, calcium ions (Ca^{2+}) and phosphate ions (PO_4^{3-}) will form an insoluble compound, calcium phosphate [$Ca_3(PO_4)_2$], while the other product, KNO_3, is soluble and remains in solution. Therefore, this is a precipitation reaction. We follow the stepwise procedure just outlined.

Step 1: The balanced molecular equation for this reaction is

$$2K_3PO_4(aq) + 3Ca(NO_3)_2(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6KNO_3(aq)$$

Step 2: To write the ionic equation, the soluble compounds are shown as dissociated ions:

$$6K^+(aq) + 2PO_4^{3-}(aq) + 3Ca^{2+}(aq) + 6NO_3^-(aq) \longrightarrow 6K^+(aq) + 6NO_3^-(aq) + Ca_3(PO_4)_2(s)$$

Step 3: Canceling the spectator ions (K^+ and NO_3^-) on each side of the equation, we obtain the net ionic equation:

$$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \longrightarrow Ca_3(PO_4)_2(s)$$

Step 4: Note that because we balanced the molecular equation first, the net ionic equation is balanced as to the number of atoms on each side and the number of positive (+6) and negative (−6) charges on the left-hand side is the same.

Properties of Acids

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

2. Cause color changes in plant dyes.

3. React with certain metals to produce hydrogen gas.

   $$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g)$$

4. React with carbonates and bicarbonates to produce carbon dioxide gas.

   $$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

5. Aqueous acid solutions conduct electricity.

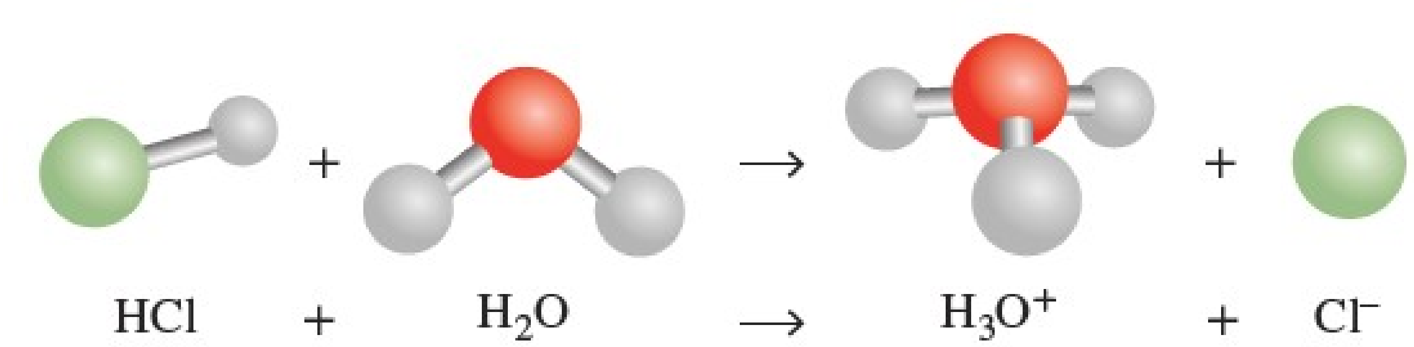
Ken Karp/McGraw-Hill

Properties of Bases

1. Have a bitter taste.
2. Feel slippery. Many soaps contain bases.
3. Cause colour changes in plant dyes.
4. Aqueous base solutions conduct electricity.

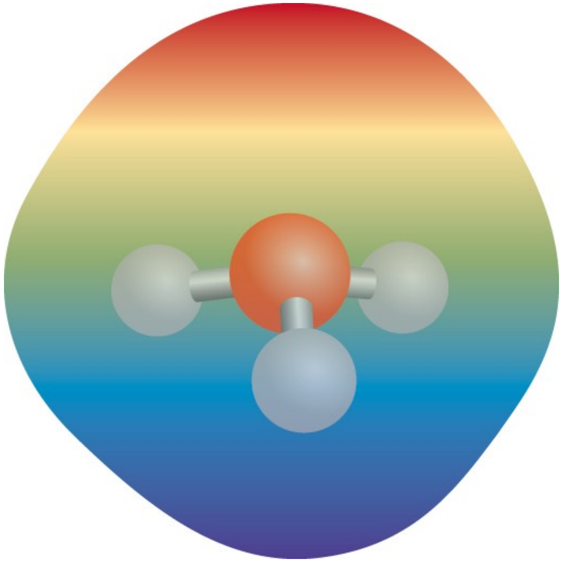
Arrhenius Acids and Bases

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



Arrhenius base is a substance that produces OH^- in water

Hydronium ion, hydrated proton, H_3O^+

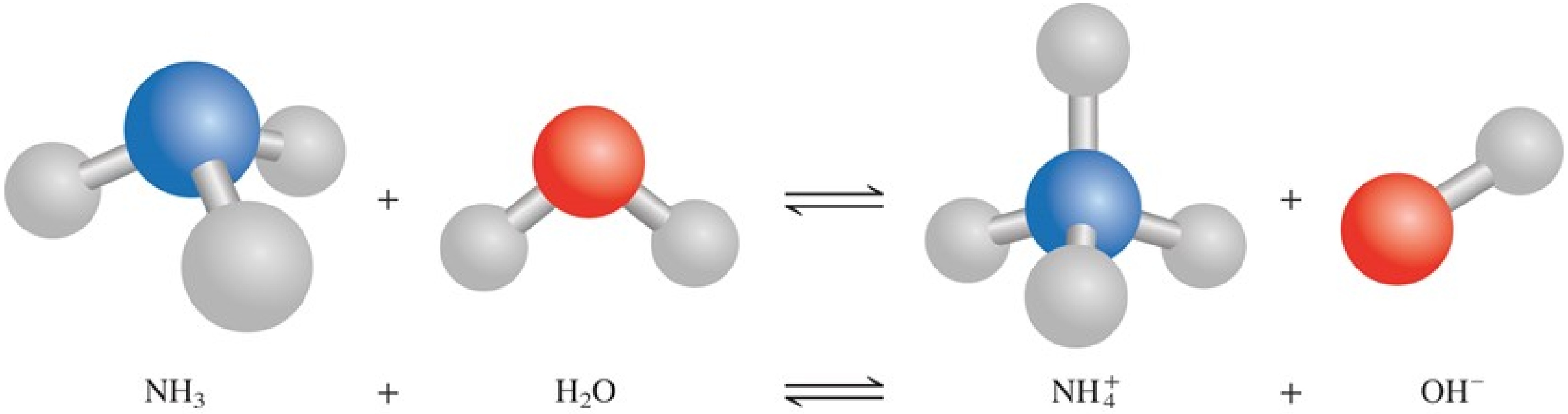


- The resulting species, H_3O^+, is known as the hydronium ion.
- The hydronium ion has a trigonal pyramidal molecular shape.
- The hydronium ion has:
  partially negative end (the O atom)
  partially positive end (the H atoms).

Brønsted Acids and Bases

A ***Brønsted acid*** is a proton donor

A ***Brønsted base*** is a proton acceptor



A Brønsted **acid** must contain at least one ionizable proton!

Types of Acids

Monoprotic **acids**

$HCl \rightarrow H^+ + Cl^-$	Strong electrolyte, strong acid
$HNO_3 \rightarrow H^+ + NO_3^-$	Strong electrolyte, strong acid
$CH_3COOH \rightarrow H^+ + CH_3COO^-$	Weak electrolyte, weak acid

Diprotic **acids**

$H_2SO_4 \rightarrow H^+ + HSO_4^-$	Strong electrolyte, strong acid
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	Weak electrolyte, weak acid

Triprotic **acids**

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	Weak electrolyte, weak acid
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	Weak electrolyte, weak acid
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	Weak electrolyte, weak acid

Common Acids

Table 4.3 Some Common Strong and Weak Acids

Strong Acids	Formula
Hydrochloric acid	HCl
Hydrobromic acid	HBr
Hydroiodic acid	HI
Nitric acid	HNO_3
Sulfuric acid	H_2SO_4
Perchloric	$HClO_4$
Weak Acids	**Formula**
Hydrofluoric acid	HF
Nitrous acid	HNO_2
Phosphoric acid	H_3PO_4
Acetic acid	CH_3COOH

EXAMPLE 4.3

Classify each of the following species in aqueous solution as a Brønsted acid or base: (a) HBr, (b) NO_2^-, (c) HCO_3^-.

Strategy What are the characteristics of a Brønsted acid? Does it contain at least an H atom? With the exception of ammonia, most Brønsted bases that you will encounter at this stage are anions.

Solution (a) We know that HCl is an acid. Because Br and Cl are both halogens (Group 7A), we expect HBr, like HCl, to ionize in water as follows:

$$HBr(aq) \longrightarrow H^+(aq) + Br^-(aq)$$

Therefore HBr is a Brønsted acid.

(b) In solution the nitrite ion can accept a proton from water to form nitrous acid:

$$NO_2^-(aq) + H^+(aq) \longrightarrow HNO_2(aq)$$

This property makes NO_2^- a Brønsted base.

(c) The bicarbonate ion is a Brønsted acid because it ionizes in solution as follows:

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

It is also a Brønsted base because it can accept a proton to form carbonic acid:

$$HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$$

Neutralization Reaction

- A ***neutralization reaction*** is a reaction between an acid and a base.
- Salt is an ionic compound made up of a cation from the base and an anion from the acid

acid + base → salt + water

$$\text{HCl}(aq) + \text{NaOH}(aq) \rightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

$$\text{H}^+(aq) + \cancel{\text{Cl}}^-(aq) + \cancel{\text{Na}}^+(aq) + \text{OH}^-(aq) \rightarrow \cancel{\text{Na}}^+(aq) + \cancel{\text{Cl}}^-(aq) + \text{H}_2\text{O}(l)$$

$$\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$$

Na^+ Cl^- are the *spectator* ions

Neutralization Reaction Involving a Weak Electrolyte

weak acid + base → salt + water

$$\mathrm{HCN}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCN}\,(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{HCN}(aq) + \cancel{\mathrm{Na}^+}\,(aq) + \mathrm{OH}^-\,(aq) \rightarrow \cancel{\mathrm{Na}^+}\,(aq) + \mathrm{CN}^-\,(aq) + \mathrm{H_2O}(l)$$

$$\mathrm{HCN}(aq) + \mathrm{OH}^-\,(aq) \rightarrow \mathrm{CN}^-\,(aq) + \mathrm{H_2O}(l)$$

Na^+ is the ***spectator*** ion

Example 4.4 1

Write molecular, ionic, and net ionic equations for each of the following acid-base reactions:

a) hydrobromic acid (*aq*) + barium hydroxide (*aq*) →

b) sulfuric acid (*aq*) + potassium hydroxide (*aq*) →

Example 4.4 3

Solution

a)

Molecular equation:

$2HBr(aq) + Ba(OH)_2(aq) \rightarrow BaBr_2(aq) + 2H_2O(l)$

Ionic equation:

$$2H^+(aq) + 2Br^-(aq) + Ba^{2+}(aq) + 2OH^-(aq) \rightarrow Ba^{2+}(aq) + 2Br^-(aq) + 2H_2O(l)$$

Net ionic equation:

$$2H^+(aq) + 2OH^-(aq) \rightarrow 2H_2O(l)$$

or

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

Both Ba^{2+} and Br^- are spectator ions.

Example 4.4 4

b)

Molecular equation:

$$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

Ionic equation:

$$H^+(aq) + HSO_4^-(aq) + 2K^+(aq) + 2OH^-(aq) \rightarrow 2K^+(aq) + SO_4^{2-}(aq) + 2H_2O(l)$$

Net ionic equation:

$$H^+(aq) + HSO_4^-(aq) + 2OH^-(aq) \rightarrow +SO_4^{2-}(aq) + 2H_2O(l)$$

Note that because HSO_4^- is a weak acid and does not ionize appreciably in water, the only spectator ion is K^+.

Neutralization Reaction Producing a Gas

Certain salts like carbonates (containing the ion), bicarbonates (containing the **H** ion), sulfites (containing the ion), and sulfides (containing the **S^{2-}** ion) react with acids to form gaseous products.

acid + base → salt + water + CO_2

$$2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O\,(l) + CO_2\,(g)$$

$$2H^+(aq) + \cancel{2Cl}^-\,(aq) + \cancel{2Na^+(aq)} + CO_3^{2-}(aq) \rightarrow \cancel{2Na^+(aq)} + \cancel{2Cl^-(aq)} + H_2O(l) + CO_2(g)$$

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

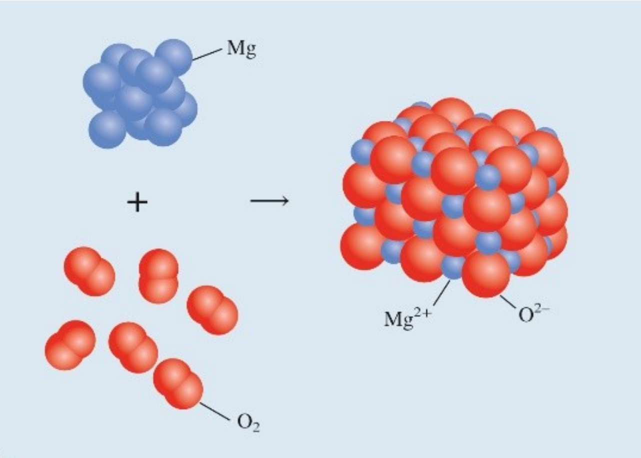
Oxidation-Reduction Reactions 1

(electron transfer reactions)

- Mg is the reducing agent because it donates electrons to oxygen and causes oxygen to be reduced
- O is the oxidizing agent, because it accepts electrons from magnesium, causing magnesium to be oxidized

$$2Mg + O_2 \rightarrow 2MgO$$

$$2Mg + O_2 + \cancel{4}e^- \rightarrow 2Mg^{2+} + 2O^{2-} + \cancel{4}e^-$$



$$2Mg \rightarrow 2Mg^{2+} + 4e^-$$ ***Oxidation*** half-reaction (lose e^-)

$$O_2 + 4e^- \rightarrow 2O^{2-}$$ ***Reduction*** half-reaction (gain e^-)

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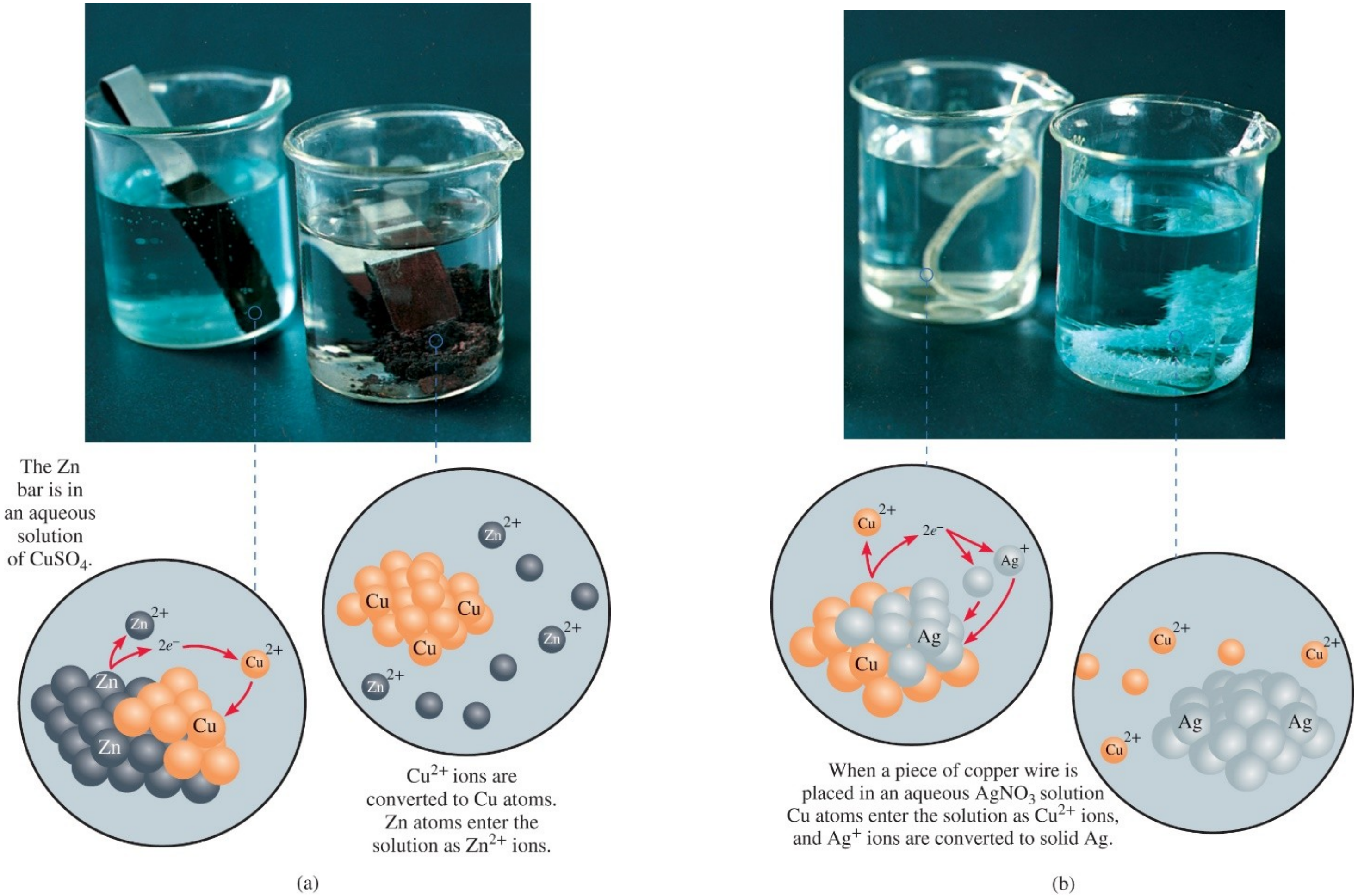
Oxidation-Reduction Reactions 2



The Zn bar is in an aqueous solution of $CuSO_4$.

Cu^{2+} ions are converted to Cu atoms. Zn atoms enter the solution as Zn^{2+} ions.

(a)

When a piece of copper wire is placed in an aqueous $AgNO_3$ solution Cu atoms enter the solution as Cu^{2+} ions, and Ag^+ ions are converted to solid Ag.

(b)

$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$

$Cu(s) + 2AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + 2Ag(s)$

Oxidation-Reduction Reactions 3

$$\text{Zn}(s) + \text{CuSO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{Cu}(s)$$

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^{-}$$

Zn is oxidized

Zn is the ***reducing agent***

$$\text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu}$$

Cu^{2+} is reduced

Cu^{2+} is the ***oxidizing agent***

Oxidation Number 1

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

Rules:

1. Free elements (uncombined state) have an oxidation number of zero.

   $Na, Be, K, Pb, H_2, O_2, P_4 = 0$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

   $$\mathrm{Li^{+}, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2}$$

3. The oxidation number of oxygen is **usually −2**
   In H_2O_2 and O_2^{2-} it is **−1**.

Oxidation Number 2

4. The oxidation number of hydrogen is +1 ***except*** when it is bonded to metals in binary compounds. In these cases, its oxidation number is −1. (e.g.; NaH)

5. Group IA metals are +1, IIA metals are +2, and fluorine is always −1. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen-for example in oxoacids and oxoanions they have positive oxidation numbers ,$HClO_3$ **(+5)**

6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion. (NH_4^+)

7. Oxidation numbers do not have to be integers. The oxidation number of oxygen in the superoxide ion, O_2^- is -1/2

EXAMPLE 4.4

Assign oxidation numbers to all the elements in the following compounds and ion: (a) Li_2O, (b) HNO_3, (c) $Cr_2O_7^{2-}$.

Solution (a) By rule 2 we see that lithium has an oxidation number of +1 (Li^+) and oxygen's oxidation number is −2 (O^{2-}).

(b) This is the formula for nitric acid, which yields a H^+ ion and a NO_3^- ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus the other group (the nitrate ion) must have a net oxidation number of −1. Oxygen has an oxidation number of −2, and if we use x to represent the oxidation number of nitrogen, then the nitrate ion can be written as

$$[N^{(x)}O_3^{(2-)}]^-$$

so that $$x + 3(-2) = -1$$

or $$x = +5$$

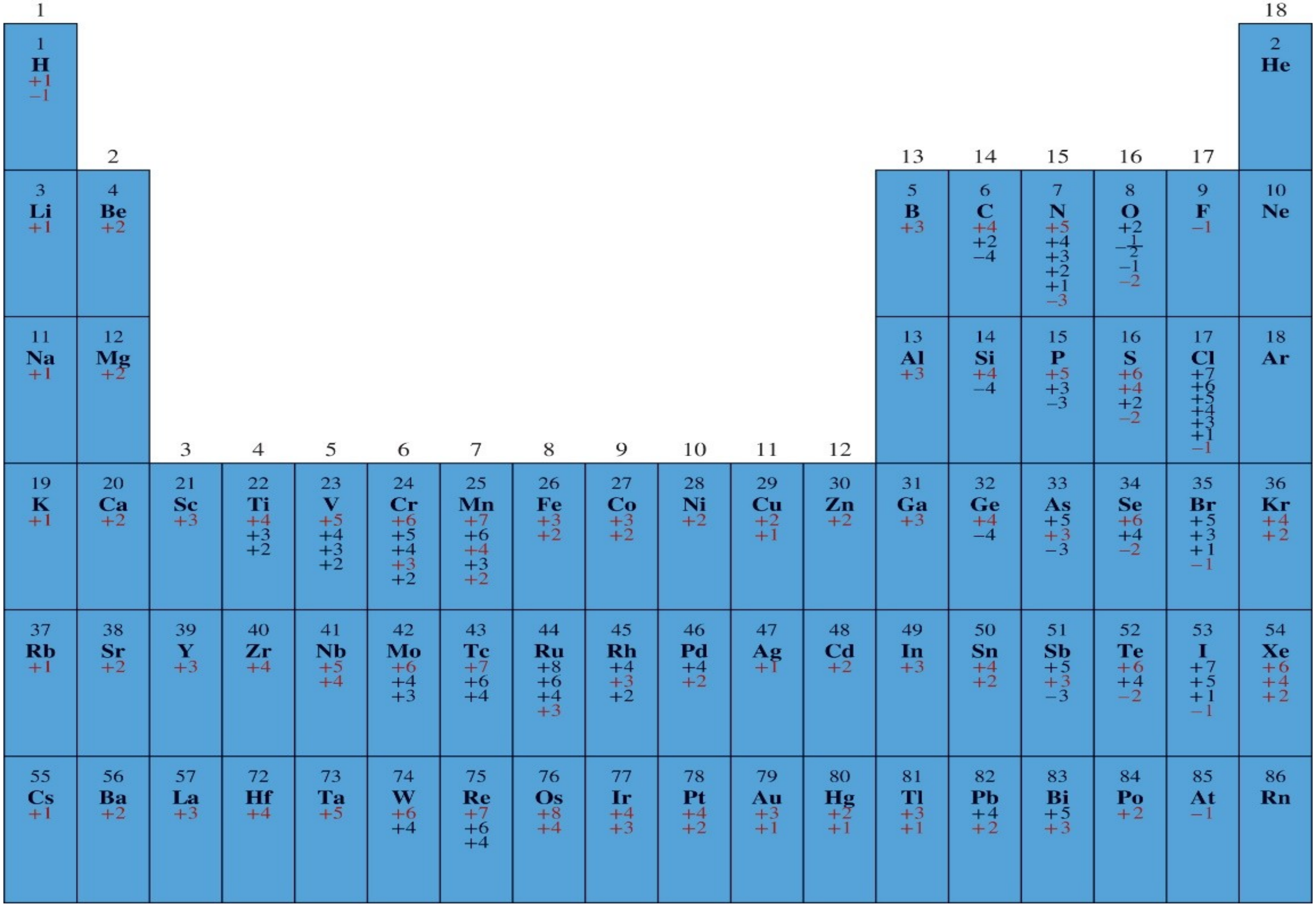
(c) From rule 6 we see that the sum of the oxidation numbers in the dichromate ion $Cr_2O_7^{2-}$ must be −2. We know that the oxidation number of O is −2, so all that remains is to determine the oxidation number of Cr, which we call y. The dichromate ion can be written as

$$[Cr_2^{(y)}O_7^{(2-)}]^{2-}$$

so that $$2(y) + 7(-2) = -2$$

or $$y = +6$$

The Oxidation Numbers of Elements in their Compounds



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** +1 −1																	2 **He**
3 **Li** +1	4 **Be** +2											5 **B** +3	6 **C** +4 +2 −4	7 **N** +5 +4 +3 +2 +1 −3	8 **O** +2 $-\frac{1}{2}$ −1 −2	9 **F** −1	10 **Ne**
11 **Na** +1	12 **Mg** +2											13 **Al** +3	14 **Si** +4 −4	15 **P** +5 +3 −3	16 **S** +6 +4 +2 −2	17 **Cl** +7 +6 +5 +4 +3 +1 −1	18 **Ar**
19 **K** +1	20 **Ca** +2	21 **Sc** +3	22 **Ti** +4 +3 +2	23 **V** +5 +4 +3 +2	24 **Cr** +6 +5 +4 +3 +2	25 **Mn** +7 +6 +4 +3 +2	26 **Fe** +3 +2	27 **Co** +3 +2	28 **Ni** +2	29 **Cu** +2 +1	30 **Zn** +2	31 **Ga** +3	32 **Ge** +4 −4	33 **As** +5 +3 −3	34 **Se** +6 +4 −2	35 **Br** +5 +3 +1 −1	36 **Kr** +4 +2
37 **Rb** +1	38 **Sr** +2	39 **Y** +3	40 **Zr** +4	41 **Nb** +5 +4	42 **Mo** +6 +4 +3	43 **Tc** +7 +6 +4	44 **Ru** +8 +6 +4 +3	45 **Rh** +4 +3 +2	46 **Pd** +4 +2	47 **Ag** +1	48 **Cd** +2	49 **In** +3	50 **Sn** +4 +2	51 **Sb** +5 +3 −3	52 **Te** +6 +4 −2	53 **I** +7 +5 +1 −1	54 **Xe** +6 +4 +2
55 **Cs** +1	56 **Ba** +2	57 **La** +3	72 **Hf** +4	73 **Ta** +5	74 **W** +6 +4	75 **Re** +7 +6 +4	76 **Os** +8 +4	77 **Ir** +4 +3	78 **Pt** +4 +2	79 **Au** +3 +1	80 **Hg** +2 +1	81 **Tl** +3 +1	82 **Pb** +4 +2	83 **Bi** +5 +3	84 **Po** +2	85 **At** −1	86 **Rn**

Types of Oxidation-Reduction Reactions₁

1) Combination Reaction: two or more substances combine to form a single product

$$A + B \rightarrow C$$

$$2\overset{0}{\text{Al}} + 3\overset{0}{\text{Br}}_2 \rightarrow 2\overset{+3}{\text{Al}}\overset{-1}{\text{Br}}_3$$

2) Decomposition Reaction: breakdown of a compound into two or more components

$$C \rightarrow A + B$$

$$2\overset{+1}{\text{K}}\overset{+5}{\text{Cl}}\overset{-2}{\text{O}}_3 \rightarrow 2\overset{+1}{\text{K}}\overset{-1}{\text{Cl}} + 3\overset{0}{\text{O}}_2$$

(Top & bottom images): Ken Karp/McGraw Hill

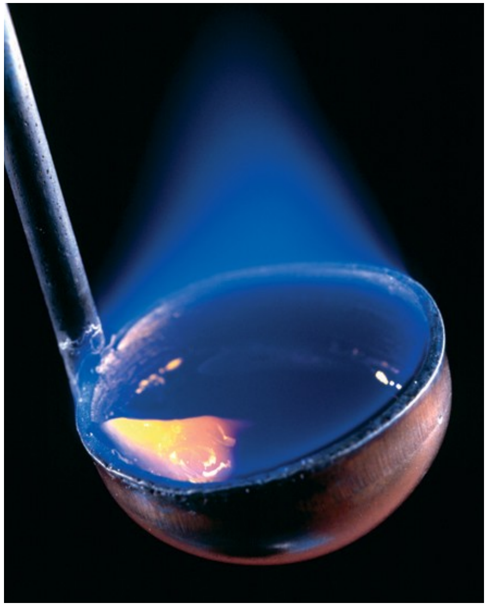
Types of Oxidation-Reduction Reactions 2

3) Combustion Reaction: in which a substance reacts with oxygen, usually with the release of heat and light to produce a flame.

$$\mathrm{A} + \mathrm{O}_2 \rightarrow \mathrm{B}$$

$$\overset{0}{\mathrm{S}} + \overset{0}{\mathrm{O}}_2 \rightarrow \overset{+4}{\mathrm{S}}\,\overset{-2}{\mathrm{O}}_2$$

$$2\,\overset{0}{\mathrm{Mg}} + \overset{0}{\mathrm{O}}_2 \rightarrow 2\,\overset{+2}{\mathrm{Mg}}\,\overset{-2}{\mathrm{O}}$$



Types of Oxidation-Reduction Reactions 3

4) Displacement Reaction: an ion (or atom) in a compound is replaced by an ion (or atom) of another element

$$\textbf{A + BC} \rightarrow \textbf{AC + B}$$

$$\overset{0}{\cancel{\mathrm{Sr}}} + 2\overset{+1}{\mathrm{H}}_2\mathrm{O} \rightarrow \overset{+2}{\mathrm{Sr}}(\mathrm{OH})_2 + \overset{0}{\mathrm{H}}_2$$

Hydrogen Displacement

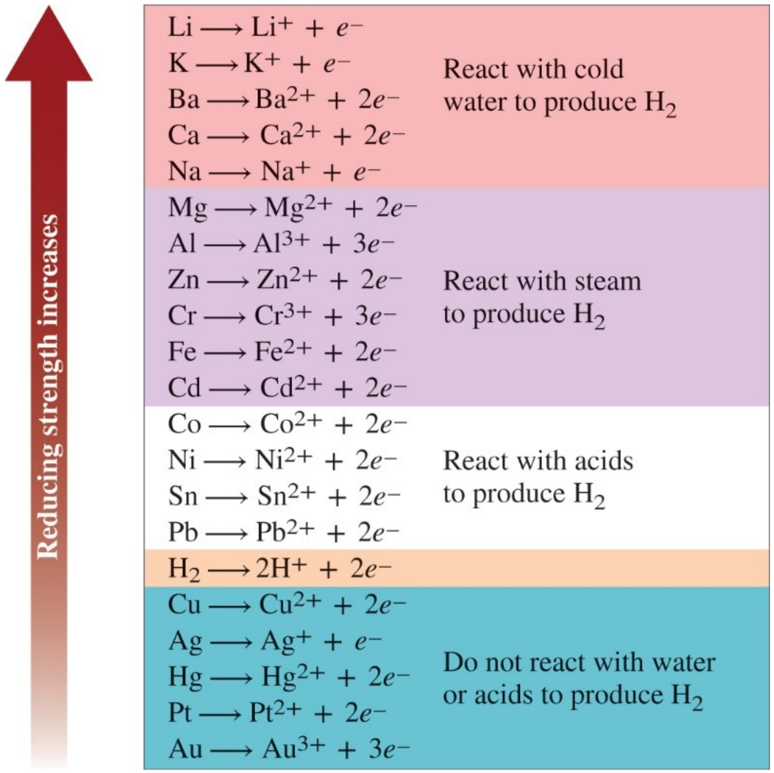
$$\overset{+4}{\mathrm{Ti}}\mathrm{Cl}_4 + 2\overset{0}{\mathrm{Mg}} \rightarrow \overset{0}{\mathrm{Ti}} + 2\overset{+2}{\mathrm{Mg}}\mathrm{Cl}_2$$

Metal Displacement

$$\overset{0}{\mathrm{Cl}}_2 + 2\mathrm{K}\overset{-1}{\mathrm{Br}} \rightarrow 2\mathrm{K}\overset{-1}{\mathrm{Cl}} + \overset{0}{\mathrm{Br}}_2$$

Halogen Displacement

The Activity Series for Metals



$Li \longrightarrow Li^{+} + e^{-}$	React with cold water to produce H_2
$K \longrightarrow K^{+} + e^{-}$	
$Ba \longrightarrow Ba^{2+} + 2e^{-}$	
$Ca \longrightarrow Ca^{2+} + 2e^{-}$	
$Na \longrightarrow Na^{+} + e^{-}$	
$Mg \longrightarrow Mg^{2+} + 2e^{-}$	React with steam to produce H_2
$Al \longrightarrow Al^{3+} + 3e^{-}$	
$Zn \longrightarrow Zn^{2+} + 2e^{-}$	
$Cr \longrightarrow Cr^{3+} + 3e^{-}$	
$Fe \longrightarrow Fe^{2+} + 2e^{-}$	
$Cd \longrightarrow Cd^{2+} + 2e^{-}$	
$Co \longrightarrow Co^{2+} + 2e^{-}$	React with acids to produce H_2
$Ni \longrightarrow Ni^{2+} + 2e^{-}$	
$Sn \longrightarrow Sn^{2+} + 2e^{-}$	
$Pb \longrightarrow Pb^{2+} + 2e^{-}$	
$H_2 \longrightarrow 2H^{+} + 2e^{-}$	
$Cu \longrightarrow Cu^{2+} + 2e^{-}$	Do not react with water or acids to produce H_2
$Ag \longrightarrow Ag^{+} + e^{-}$	
$Hg \longrightarrow Hg^{2+} + 2e^{-}$	
$Pt \longrightarrow Pt^{2+} + 2e^{-}$	
$Au \longrightarrow Au^{3+} + 3e^{-}$	

<u>Hydrogen Displacement Reaction</u>

M + BC → MC + B

M is metal

BC is acid or H_2O

B is H_2

$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$

~~$Pb + 2H_2O \rightarrow Pb(OH)_2 + H_2$~~

Access the text alternative for slide images.

The Activity Series for Halogens

$$F_2 > Cl_2 > Br_2 > I_2$$

Halogen Displacement Reaction

$$\overset{0}{Cl_2} + 2K\overset{-1}{Br} \rightarrow 2K\overset{-1}{Cl} + \overset{0}{Br_2}$$

~~$I_2 + 2KBr \rightarrow 2KI + Br_2$~~

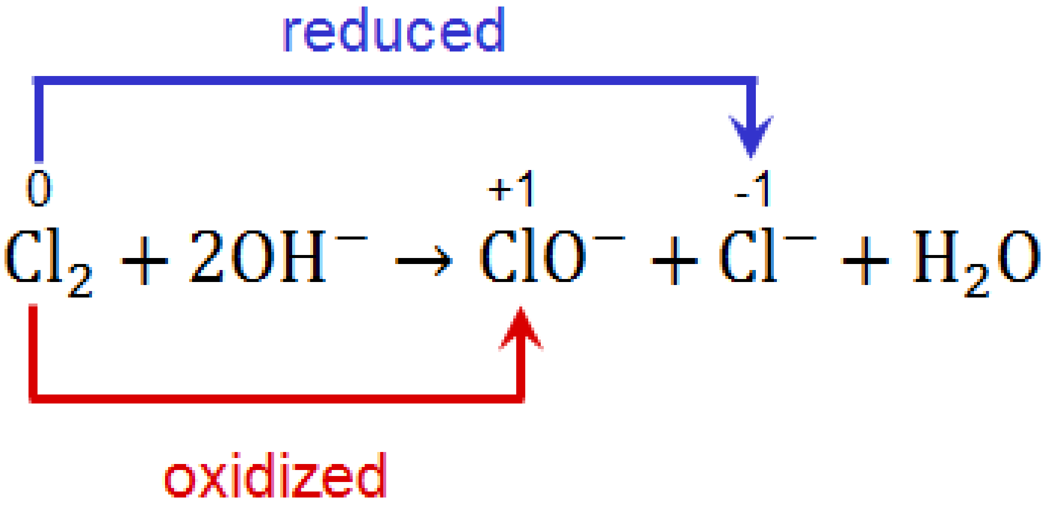
Stephen Frisch/McGraw Hill

Types of Oxidation-Reduction Reactions

4

5) Disproportionation Reaction: the same element is simultaneously oxidized and reduced.

Example:



$$\overset{0}{Cl_2} + 2OH^- \rightarrow \overset{+1}{Cl}O^- + \overset{-1}{Cl^-} + H_2O$$

EXAMPLE 4.5

Classify the following redox reactions and indicate changes in the oxidation numbers of the elements:

(a) $2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$

(b) $6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$

(c) $Ni(s) + Pb(NO_3)_2(aq) \longrightarrow Pb(s) + Ni(NO_3)_2(aq)$

(d) $2NO_2(g) + H_2O(l) \longrightarrow HNO_2(aq) + HNO_3(aq)$

Strategy Review the definitions of combination reactions, decomposition reactions, displacement reactions, and disproportionation reactions.

Solution (a) This is a decomposition reaction because one reactant is converted to two different products. The oxidation number of N changes from +1 to 0, while that of O changes from −2 to 0.

(b) This is a combination reaction (two reactants form a single product). The oxidation number of Li changes from 0 to +1 while that of N changes from 0 to −3.

(c) This is a metal displacement reaction. The Ni metal replaces (reduces) the Pb^{2+} ion. The oxidation number of Ni increases from 0 to +2 while that of Pb decreases from +2 to 0.

(d) The oxidation number of N is +4 in NO_2 and it is +3 in HNO_2 and +5 in HNO_3. Because the oxidation number of the *same* element both increases and decreases, this is a disproportionation reaction.

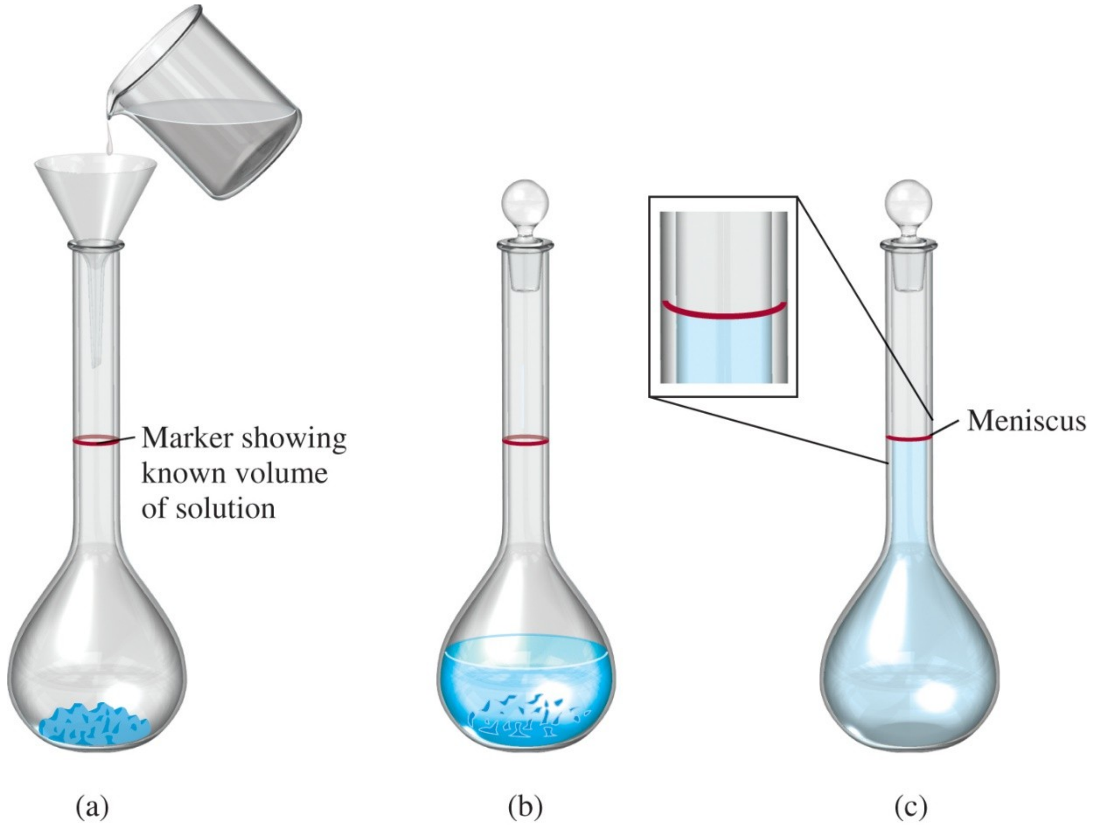
Solution Stoichiometry

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Molarity (M), or **molar concentration,** which is the number of moles of solute per liter of solution

$$M = \text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Preparing a Solution of Known Concentration



EXAMPLE 4.6

How many grams of potassium dichromate ($K_2Cr_2O_7$) are required to prepare a 250-mL solution whose concentration is 2.16 *M*?

Strategy How many moles of $K_2Cr_2O_7$ does a 1-L (or 1000 mL) 2.16 *M* $K_2Cr_2O_7$ solution contain? A 250-mL solution? How would you convert moles to grams?

Solution The first step is to determine the number of moles of $K_2Cr_2O_7$ in 250 mL or 0.250 L of a 2.16 *M* solution. Rearranging Equation (4.1) gives

$$\text{moles of solute} = \text{molarity} \times \text{L soln}$$

Thus,

$$\begin{aligned}\text{moles of } K_2Cr_2O_7 &= \frac{2.16 \text{ mol } K_2Cr_2O_7}{1 \cancel{\text{L soln}}} \times 0.250 \cancel{\text{L soln}} \\ &= 0.540 \text{ mol } K_2Cr_2O_7\end{aligned}$$

The molar mass of $K_2Cr_2O_7$ is 294.2 g, so we write

$$\begin{aligned}\text{grams of } K_2Cr_2O_7 \text{ needed} &= 0.540 \cancel{\text{mol } K_2Cr_2O_7} \times \frac{294.2 \text{ g } K_2Cr_2O_7}{1 \cancel{\text{mol } K_2Cr_2O_7}} \\ &= 159 \text{ g } K_2Cr_2O_7\end{aligned}$$

Ken Karp/McGraw-Hill

EXAMPLE 4.7

In a biochemical assay, a chemist needs to add 3.81 g of glucose to a reaction mixture. Calculate the volume in milliliters of a 2.53 *M* glucose solution she should use for the addition.

Strategy We must first determine the number of moles contained in 3.81 g of glucose and then use Equation (4.2) to calculate the volume.

Solution From the molar mass of glucose, we write

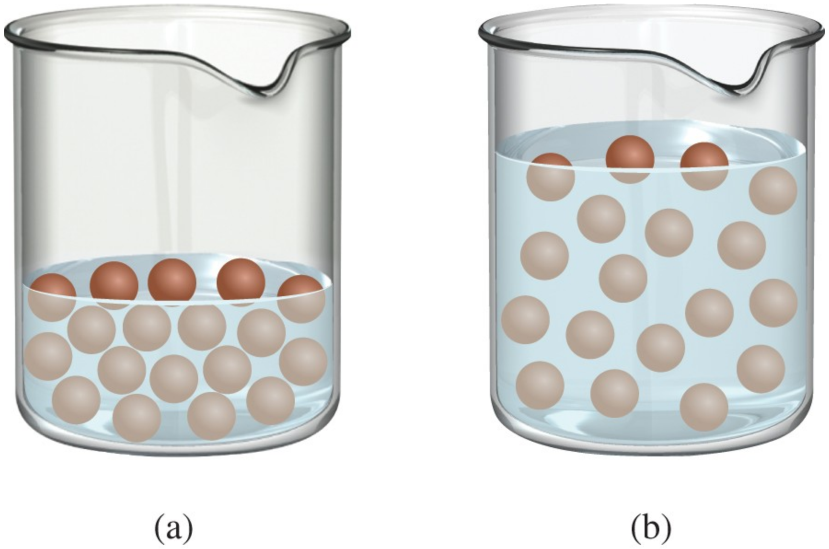
$$3.81\ \cancel{\mathrm{g\ C_6H_{12}O_6}} \times \frac{1\ \mathrm{mol\ C_6H_{12}O_6}}{180.2\ \cancel{\mathrm{g\ C_6H_{12}O_6}}} = 2.114 \times 10^{-2}\ \mathrm{mol\ C_6H_{12}O_6}$$

Next, we calculate the volume of the solution that contains 2.114×10^{-2} mole of the solute. Rearranging Equation (4.2) gives

$$\begin{aligned} V &= \frac{n}{M} \\ &= \frac{2.114 \times 10^{-2}\ \mathrm{mol\ C_6H_{12}O_6}}{2.53\ \mathrm{mol\ C_6H_{12}O_6/L\ soln}} \times \frac{1000\ \mathrm{mL\ soln}}{1\ \mathrm{L\ soln}} \\ &= \boxed{8.36\ \mathrm{mL\ soln}} \end{aligned}$$

Dilution

Dilution is the procedure for preparing a less concentrated solution from a more concentrated solution.


(a) (b)

Moles of solute before dilution (i) = Moles of solute after dilution (f)

$$M_i V_i = M_f V_f$$

EXAMPLE 4.8

Describe how you would prepare 5.00×10^2 mL of a 1.75 *M* H_2SO_4 solution, starting with an 8.61 *M* stock solution of H_2SO_4.

Strategy Because the concentration of the final solution is less than that of the original one, this is a dilution process. Keep in mind that in dilution, the concentration of the solution decreases but the number of moles of the solute remains the same.

Solution We prepare for the calculation by tabulating our data:

$$\begin{aligned} M_\text{i} &= 8.61\ M & \qquad M_\text{f} &= 1.75\ M \\ V_\text{i} &= ? & V_\text{f} &= 5.00 \times 10^2\ \text{mL} \end{aligned}$$

Substituting in Equation (4.3),

$$\begin{aligned} (8.61\ M)(V_\text{i}) &= (1.75\ M)(5.00 \times 10^2\ \text{mL}) \\ V_\text{i} &= \frac{(1.75\ M)(5.00 \times 10^2\ \text{mL})}{8.61\ M} \\ &= 102\ \text{mL} \end{aligned}$$

Thus, we must dilute 102 mL of the 8.61 *M* H_2SO_4 solution with sufficient water to give a final volume of 5.00×10^2 mL in a 500-mL volumetric flask to obtain the desired concentration.

Gravimetric Analysis

Analytical technique based on the measurement of mass

1. Dissolve unknown substance in water
2. React unknown with known substance to form a **precipitate**
3. Filter and dry precipitate
4. Weigh precipitate
5. Use chemical formula and mass of precipitate to determine amount of unknown ion

(Left, middle, and right images): Ken Karp/McGraw-Hill

EXAMPLE 4.9

A 0.5662-g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with an excess of $AgNO_3$. If 1.0882 g of AgCl precipitate forms, what is the percent by mass of Cl in the original compound?

Solution The molar masses of Cl and AgCl are 35.45 g and 143.4 g, respectively. Therefore, the percent by mass of Cl in AgCl is given by

$$\begin{aligned} \%\text{Cl} &= \frac{35.45\text{ g Cl}}{143.4\text{ g AgCl}} \times 100\% \\ &= 24.72\% \end{aligned}$$

Next, we calculate the mass of Cl in 1.0882 g of AgCl. To do so we convert 24.72 percent to 0.2472 and write

$$\begin{aligned} \text{mass of Cl} &= 0.2472 \times 1.0882\text{ g} \\ &= 0.2690\text{ g} \end{aligned}$$

Because the original compound also contained this amount of Cl^- ions, the percent by mass of Cl in the compound is

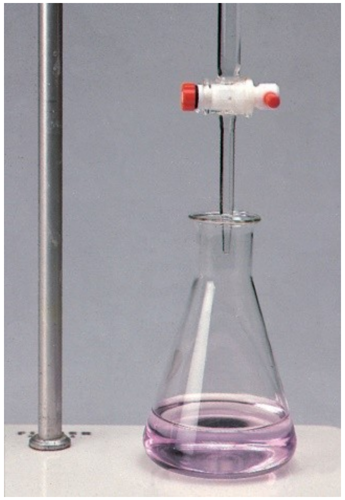
$$\begin{aligned} \%\text{Cl} &= \frac{0.2690\text{ g}}{0.5662\text{ g}} \times 100\% \\ &= \boxed{47.51\%} \end{aligned}$$

Titrations 1

- In a **titration,** a solution of accurately known concentration (**standard solution**) is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.
- **Equivalence point**: the point at which the reaction is complete.
- **Indicator**: substance that changes colour at the equivalence point.

Slowly add base to unknown acid UNTIL

the indicator changes colour

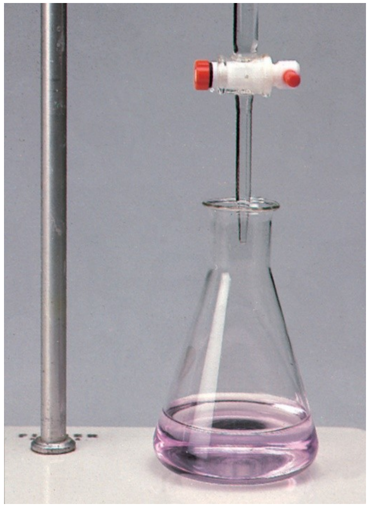


Titrations 2

Titrations can be used in the analysis of:

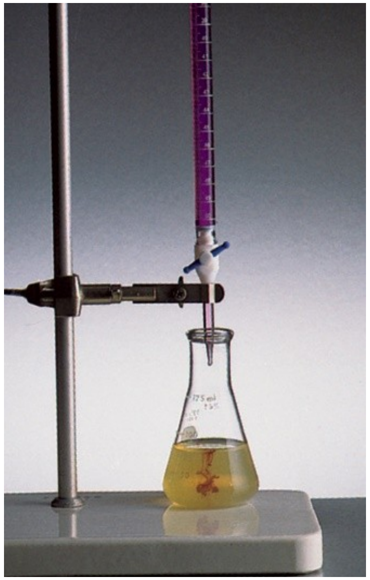
1) Acid-base reactions

$H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$



2) Redox reactions

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$



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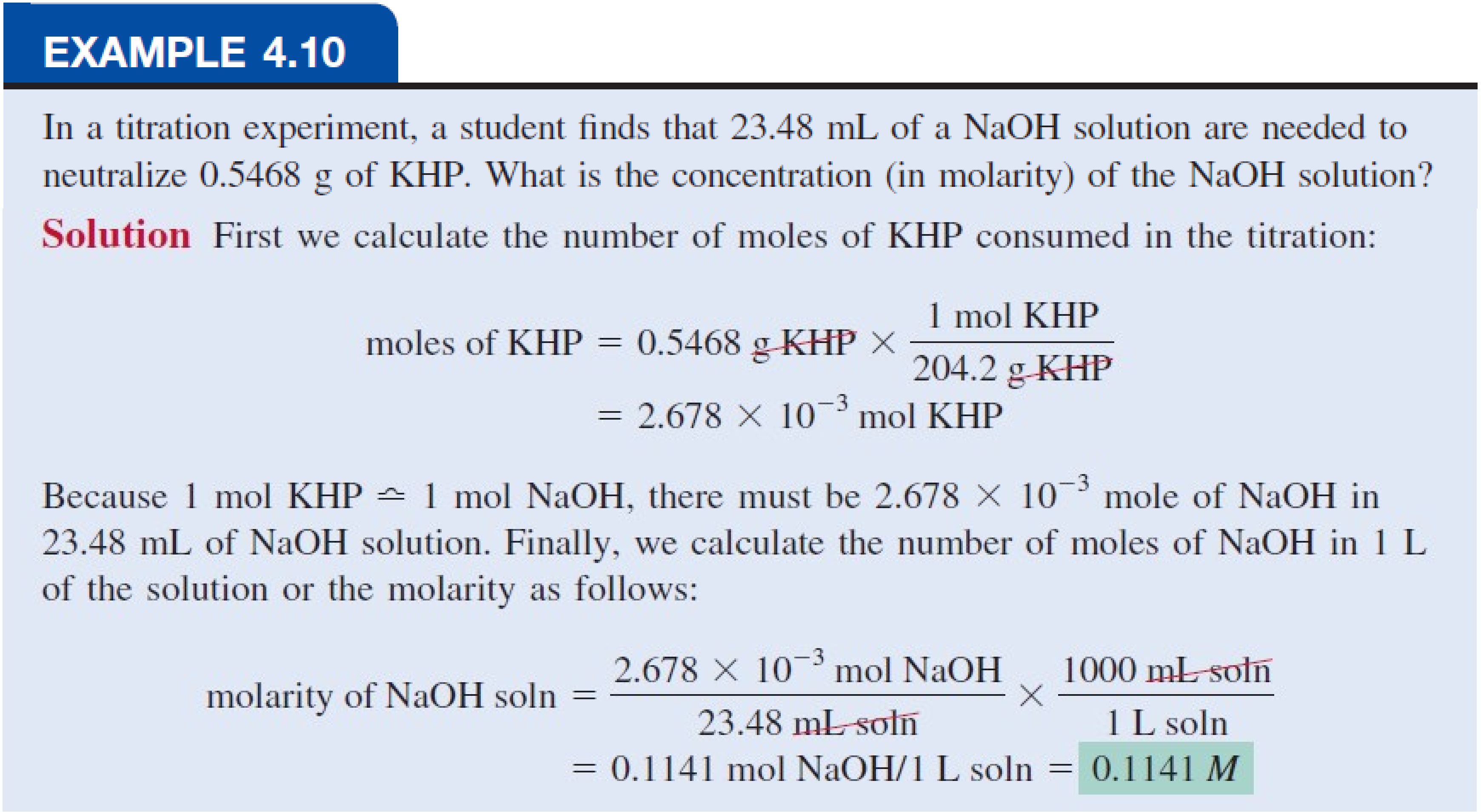

EXAMPLE 4.10

In a titration experiment, a student finds that 23.48 mL of a NaOH solution are needed to neutralize 0.5468 g of KHP. What is the concentration (in molarity) of the NaOH solution?

Solution First we calculate the number of moles of KHP consumed in the titration:

$$\begin{aligned}\text{moles of KHP} &= 0.5468\ \cancel{\text{g KHP}} \times \frac{1\ \text{mol KHP}}{204.2\ \cancel{\text{g KHP}}}\\ &= 2.678 \times 10^{-3}\ \text{mol KHP}\end{aligned}$$

Because 1 mol KHP $\bumpeq$ 1 mol NaOH, there must be 2.678×10^{-3} mole of NaOH in 23.48 mL of NaOH solution. Finally, we calculate the number of moles of NaOH in 1 L of the solution or the molarity as follows:

$$\begin{aligned}\text{molarity of NaOH soln} &= \frac{2.678 \times 10^{-3}\ \text{mol NaOH}}{23.48\ \cancel{\text{mL soln}}} \times \frac{1000\ \cancel{\text{mL soln}}}{1\ \text{L soln}}\\ &= 0.1141\ \text{mol NaOH/1 L soln} = \boxed{0.1141\ M}\end{aligned}$$

KHP= Potassium hydrogen phthalate ($C_8H_5KO_4$)

EXAMPLE 4.11

How many milliliters (mL) of a 0.610 *M* NaOH solution are needed to neutralize 20.0 mL of a 0.245 *M* H_2SO_4 solution?

Solution First we calculate the number of moles of H_2SO_4 in a 20.0 mL solution:

$$\text{moles } H_2SO_4 = \frac{0.245 \text{ mol } H_2SO_4}{1000 \cancel{\text{ mL soln}}} \times 20.0 \cancel{\text{ mL soln}}$$
$$= 4.90 \times 10^{-3} \text{ mol } H_2SO_4$$

From the stoichiometry we see that 1 mol $H_2SO_4 \mathrel{\widehat{=}} 2$ mol NaOH. Therefore, the number of moles of NaOH reacted must be $2 \times 4.90 \times 10^{-3}$ mole, or 9.80×10^{-3} mole. From the definition of molarity [see Equation (4.1)], we have

$$\text{liters of soln} = \frac{\text{moles of solute}}{\text{molarity}}$$

or

$$\text{volume of NaOH} = \frac{9.80 \times 10^{-3} \text{ mol NaOH}}{0.610 \text{ mol/L soln}}$$
$$= 0.0161 \text{ L or } 16.1 \text{ mL}$$

EXAMPLE 4.12

A 16.42-mL volume of 0.1327 *M* $KMnO_4$ solution is needed to oxidize 25.00 mL of a $FeSO_4$ solution in an acidic medium. What is the concentration of the $FeSO_4$ solution in molarity? The net ionic equation is

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Solution The number of moles of $KMnO_4$ in 16.42 mL of the solution is

$$\begin{aligned} \text{moles of } KMnO_4 &= \frac{0.1327 \text{ mol } KMnO_4}{1000 \cancel{\text{ mL soln}}} \times 16.42 \cancel{\text{ mL}} \\ &= 2.179 \times 10^{-3} \text{ mol } KMnO_4 \end{aligned}$$

From the net ionic equation we see that 5 mol $Fe^{2+} \bumpeq$ 1 mol MnO_4^-. Therefore, the number of moles of $FeSO_4$ oxidized is

$$\begin{aligned} \text{moles } FeSO_4 &= 2.179 \times 10^{-3} \cancel{\text{ mol } KMnO_4} \times \frac{5 \text{ mol } FeSO_4}{1 \cancel{\text{ mol } KMnO_4}} \\ &= 1.090 \times 10^{-2} \text{ mol } FeSO_4 \end{aligned}$$

The concentration of the $FeSO_4$ solution in moles of $FeSO_4$ per liter of solution is

$$\begin{aligned} \text{molarity of } FeSO_4 &= \frac{\text{mol } FeSO_4}{\text{L soln}} \\ &= \frac{1.090 \times 10^{-2} \text{ mol } FeSO_4}{25.00 \cancel{\text{ mL soln}}} \times \frac{1000 \cancel{\text{ mL soln}}}{1 \text{ L soln}} \\ &= 0.4360\ M \end{aligned}$$

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