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Chapter 4

# Reactions in Aqueous Solutions

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### 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.

<u>Solution</u>	Solvent	<u>Solute</u>
Soft drink (1)	H <sub>2</sub> O	Sugar, CO <sub>2</sub>
Air (g)	N <sub>2</sub>	O <sub>2</sub> , Ar, CH <sub>4</sub>
Soft solder (s)	Pb	Sn



aqueous solutions of KMnO<sub>4</sub>

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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.



nonelectrolyte



weak electrolyte



strong electrolyte

Conduct electricity in solution? Cations (+) and Anions (-)

Strong Electrolyte – 100% dissociation

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

Weak Electrolyte – not completely dissociated

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

*Ionization* of acetic acid

$$CH_3COOH(aq) \Box CH_3COO^-(aq) + H^+(aq)$$

 $\rightleftharpoons$  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.





# 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 <sub>3</sub> COOH	$(NH_2)_2CO$ (urea)
HNO <sub>3</sub>	HF	CH <sub>3</sub> OH (methanol)
HClO <sub>4</sub>	HNO <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> OH (ethanol)
H <sub>2</sub> SO <sub>4</sub> *	NH <sub>3</sub>	$C_6H_{12}O_6$ (glucose)
NaOH	$H_2O^{\dagger}$	$C_{12}H_{22}O_{11}$ (sucrose)
Ba(OH) <sub>2</sub>		
Ionic compounds		

 $^{*}H_{2}SO_{4}$  has two ionizable H<sup>+</sup> ions, but only one of the H<sup>+</sup> ions is totally ionized.

<sup>†</sup>Pure water is an extremely weak electrolyte.

#### **Precipitation Reactions**

Precipitate – insoluble solid that separates from solution.

 $Pb(NO_3)_2(aq) + 2NaI(aq) \rightarrow PbI_2(s) + 2NaNO_3(aq)$ *molecular equation* 

 $Pb^{2+}(aq) + 2NO_{3}^{-}(aq) + 2Na^{+}(aq) + 2I^{-}(aq) \rightarrow PbI_{2}(s) + 2Na^{+}(aq) + 2NO_{3}^{-}(aq)$ 

ionic equation

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

net ionic equation

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



PbI<sub>2</sub>

### Precipitation of Lead Iodide



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

PbI<sub>2</sub>

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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 $\left( NH_{4}^{+} \right)$	
Nitrates $NO_3^-$ , acetates (CH <sub>3</sub> COO <sup>-</sup> ),	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 <sup>-</sup> )	Compounds containing alkali metal ions and the $Ba^{2+}$ ion

### Examples of Insoluble Compounds



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

## 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**.

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

**Strategy** Although it is not necessary to memorize the solubilities of compounds, you should keep in mind the following useful rules: all ionic compounds containing alkali metal cations; the ammonium ion; and the nitrate, bicarbonate, and chlorate ions are soluble. For other compounds, we need to refer to Table 4.2.

**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<sub>3</sub> is insoluble.

(c) Sodium is an alkali metal (Group 1A) so Na<sub>3</sub>PO<sub>4</sub> is soluble.

Predict what happens when a potassium phosphate ( $K_3PO_4$ ) solution is mixed with a calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>] 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<sub>3</sub>)<sub>2</sub> dissociates into Ca<sup>2+</sup> and NO<sub>3</sub><sup>-</sup> ions. According to Table 4.2, calcium ions (Ca<sup>2+</sup>) and phosphate ions (PO<sub>4</sub><sup>3^-</sup>) will form an insoluble compound, calcium phosphate [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], while the other product, KNO<sub>3</sub>, 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

$$2K_{3}PO_{4}(aq) + 3Ca(NO_{3})_{2}(aq) \longrightarrow Ca_{3}(PO_{4})_{2}(s) + 6KNO_{3}(aq)$$

Step 2: To write the ionic equation, the soluble compounds are shown as dissociated ions:  $6K^+(aa) + 2PO_4^{3-}(aa) + 3Ca^{2+}(aa) + 6NO_2^{-}(aa) \longrightarrow$ 

$$6K^{+}(aq) + 2PO_{4}^{3}(aq) + 3Ca^{2+}(aq) + 6NO_{3}(aq) \longrightarrow$$
  
$$6K^{+}(aq) + 6NO_{3}^{-}(aq) + Ca_{3}(PO_{4})_{2}(s)$$

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

$$3\operatorname{Ca}^{2+}(aq) + 2\operatorname{PO}_4^{3-}(aq) \longrightarrow \operatorname{Ca}_3(\operatorname{PO}_4)_2(s)$$

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.

#### Chemistry In Action: An Undesirable Precipitation Reaction

 $Ca^{2+}(aq) + 2HCO_{3}^{-}(aq) \stackrel{\bullet}{\rightarrow} CaCO_{3}(s) + CO_{2}(aq) + H_{2}O(I)$  $CO_{2}(aq) \stackrel{\bullet}{\rightarrow} CO_{2}(g)$ 

**Boiler Scale Deposits** 



### Properties of Acids

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

Cause color changes in plant dyes.

React with certain metals to produce hydrogen gas.

 $2\text{HCl}(aq) + \text{Mg}(s) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)$ 

React with carbonates and bicarbonates to produce carbon dioxide gas.

 $2\mathrm{HCl}(aq) + \mathrm{CaCO}_3(s) \rightarrow \mathrm{CaCl}_2(aq) + \mathrm{CO}_2(g) + \mathrm{H}_2\mathrm{O}(h)$ 

Aqueous acid solutions conduct electricity.



#### Properties of Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

Cause color changes in plant dyes.

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<sup>-</sup> in water.

### Hydronium ion, hydrated proton, $H_3O^+$



#### 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

 $HCl \rightarrow H^{+} + Cl^{-}$  $HNO_{3} \rightarrow H^{+} + NO_{3}^{-}$  $CH_{3}COOH \rightarrow H^{+} + CH_{3}COO^{-}$ 

**Diprotic** acids  $H_2SO_4 \rightarrow H^+ + HSO_4^ HSO_4^- \square H^+ + SO_4^{2-}$ 

#### Triprotic acids

 $H_{3}PO_{4} \Box H^{+} + H_{2}PO_{4}^{-}$  $H_{2}PO_{4}^{-} \Box H^{+} + HPO_{4}^{2-}$  $HPO_{4}^{2-} \Box H^{+} + PO_{4}^{3-}$ 

Strong electrolyte, strong acid Strong electrolyte, strong acid Weak electrolyte, weak acid

Strong electrolyte, strong acid Weak electrolyte, weak acid

Weak electrolyte, weak acid Weak electrolyte, weak acid 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 <sub>3</sub>
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>
Perchloric	HClO <sub>4</sub>
Weak Acids	Formula
Hydrofluoric acid	HF
Nitrous acid	HNO <sub>2</sub>
Phosphoric acid	H <sub>3</sub> PO <sub>4</sub>
Acetic acid	CH <sub>3</sub> COOH

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:

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

Therefore HBr is a Brønsted acid.

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

$$\mathrm{NO}_2^-(aq) + \mathrm{H}^+(aq) \longrightarrow \mathrm{HNO}_2(aq)$$

This property makes  $NO_2^-$  a Brønsted base.

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

$$\operatorname{HCO}_{3}^{-}(aq) \rightleftharpoons \operatorname{H}^{+}(aq) + \operatorname{CO}_{3}^{2-}(aq)$$

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

$$\operatorname{HCO}_{3}^{-}(aq) + \operatorname{H}^{+}(aq) \rightleftharpoons \operatorname{H}_{2}\operatorname{CO}_{3}(aq)$$

#### Neutralization Reaction

#### acid + base $\rightarrow$ salt + water

 $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ 

 $H^{+}(aq) + \pounds^{-}(aq) + \aleph^{+}(aq) + OH^{-}(aq) \rightarrow$  $\aleph^{+}(aq) + \pounds^{-}(aq) + \mu_{2}O(l)$ 

#### $\mathrm{H}^{+}(aq) + \mathrm{OH}^{-}(aq) \rightarrow \mathrm{H}_{2}\mathrm{O}(l)$

## Neutralization Reaction Involving a Weak Electrolyte

weak acid + base  $\rightarrow$  salt + water

 $HCN(aq) + NaOH(aq) \rightarrow NaCN(aq) + H_2O(l)$ 

 $\mathrm{HCN}(aq) + \mathrm{Na}^{+}(aq) + \mathrm{OH}^{-}(aq) \to \mathrm{Na}^{+}(aq) + \mathrm{CN}^{-}(aq) + \mathrm{H}_{2}\mathrm{O}(l)$ 

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

#### 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  $(aq) \rightarrow$
- b) sulfuric acid (aq) + potassium hydroxide  $(aq) \rightarrow$

#### Example 4.4 3

#### Solution

a) Molecular equation:

 $2\text{HBr}(aq) + \text{Ba}(\text{OH})_2(aq) \rightarrow \text{BaBr}_2(aq) + 2\text{H}_2\text{O}(l)$ 

Ionic equation:

 $2H^{+}(aq)+2Br^{-}(aq)+Ba^{2+}(aq)+2OH^{-}(aq) \rightarrow Ba^{2+}(aq)+2Br^{-}(aq)+2H_{2}O(l)$ Net ionic equation:  $2H^{+}(aq)+2OH^{-}(aq) \rightarrow 2H_{2}O(l)$ or  $H^{+}(aq)+OH^{-}(aq) \rightarrow H_{2}O(l)$ Both Ba<sup>2+</sup> and Br<sup>-</sup> 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:

$$\mathrm{H}^{+}(aq) + \mathrm{HSO}_{4}^{-}(aq) + 2\mathrm{K}^{+}(aq) + 2\mathrm{OH}^{-}(aq) \rightarrow 2\mathrm{K}^{+}(aq) + \mathrm{SO}_{4}^{2-}(aq) + 2\mathrm{H}_{2}\mathrm{O}(l)$$

Net ionic equation:

$$\mathrm{H}^{+}(aq) + \mathrm{HSO}_{4}^{-}(aq) + 2\mathrm{OH}^{-}(aq) \rightarrow +\mathrm{SO}_{4}^{2-}(aq) + 2\mathrm{H}_{2}\mathrm{O}(l)$$

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

#### Neutralization Reaction Producing a Gas

#### acid + base $\rightarrow$ salt + water + CO<sub>2</sub>

 $2\text{HCl}(aq) + \text{Na}_2\text{CO}_3(aq) \rightarrow 2\text{NaCl}(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$ 

 $2\mathrm{H}^{+}(aq) + 2\mathrm{Cl}^{-}(aq) + 2\mathrm{Na}^{+}(aq) + \mathrm{CO}_{3}^{2-}(aq) \rightarrow 2\mathrm{Na}^{+}(aq) + 2\mathrm{Cl}^{+}(aq) + \mathrm{H}_{2}\mathrm{O}(l) + \mathrm{CO}_{2}(g)$ 

 $2\mathrm{H}^{+}(aq) + \mathrm{CO}_{3}^{2-}(aq) \rightarrow \mathrm{H}_{2}\mathrm{O}(l) + \mathrm{CO}_{2}(g)$ 

#### Oxidation-Reduction Reactions 1





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

$$O_{2} + 4e^{-} \rightarrow 2O^{2-}$$
  

$$Reduction half-reaction (gain e^{-})$$
  

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

$$2Mg + O_{2} \rightarrow 2MgO$$

#### Oxidation-Reduction Reactions 2



#### Oxidation-Reduction Reactions 3

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

 $Zn \rightarrow Zn^{2+} + 2e^{-}$  Zn is oxidized

Zn is the *reducing agent* 

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

Cu<sup>2+</sup> is reduced

Cu<sup>2+</sup> 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.

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.

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

3. The oxidation number of oxygen is **usually** -2. In H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub><sup>2-</sup> 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.
- 5. Group IA metals are +1, IIA metals are +2, and fluorine is always -1.
- 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.
- 7. Oxidation numbers do not have to be integers. The oxidation number of oxygen in the superoxide ion,

$$O_2^-$$
, is  $-\frac{1}{2}$ .

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<sup>+</sup>) 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

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

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

or

$$y = +6$$

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# The Oxidation Numbers of Elements in their Compounds

1																	18
1 H +1 -1	2											12	14	15	16	17	2 He
	2	8									-	15	14	15	10	17	
3 Li +1	4 Be +2											5 <b>B</b> +3	6 C +4 +2 -4	7 $\mathbf{X}_{+5}^{+5}$ +43 +22 +1 -3		9 F -1	10 Ne
11 Na +1	12 <b>Mg</b> +2	3	4	5	6	7	Q	0	10	11	12	13 <b>Al</b> +3	14 <b>Si</b> +4 -4	15 <b>P</b> +5 +3 -3	16 <b>S</b> +6 +4 +2 -2	17 <b>Cl</b> +76 +43 +31 -1	18 <b>Ar</b>
10	20	21			21	25	~	27	10		12	21	22	22	24	25	26
19 K +1	20 Ca +2	21 Sc +3	22 <b>Ti</b> +4 +3 +2	23 <b>V</b> +5 +4 +3 +2	24 <b>Cr</b> +6 +5 +4 +3 +2	25 <b>Mn</b> +7 +6 +4 +3 +2	26 Fe +3 +2	27 Co +3 +2	28 Ni +2	29 Cu +2 +1	30 <b>Zn</b> +2	31 Ga +3	32 Ge +4 -4	33 <b>As</b> +5 +3 -3	34 <b>Se</b> +6 +4 -2	35 <b>Br</b> +5 +3 +1 -1	36 <b>Kr</b> +4 +2
37 <b>Rb</b> +1	38 <b>Sr</b> +2	39 <b>Y</b> +3	40 <b>Zr</b> +4	41 <b>Nb</b> +5 +4	42 <b>Mo</b> +6 +4 +3	43 <b>Tc</b> +7 +6 +4	44 <b>Ru</b> +8 +6 +4 +3	45 <b>Rh</b> +4 +3 +2	46 <b>Pd</b> +4 +2	47 Ag +1	48 <b>Cd</b> +2	49 <b>In</b> +3	50 <b>Sn</b> +4 +2	51 <b>Sb</b> +5 +3 -3	52 <b>Te</b> +6 +4 -2	53 I +7 +5 +1 -1	54 <b>Xe</b> +6 +4 +2
55 Cs +1	56 <b>Ba</b> +2	57 <b>La</b> +3	72 <b>Hf</b> +4	73 <b>Ta</b> +5	74 <b>W</b> +6 +4	75 <b>Re</b> +7 +6 +4	76 <b>Os</b> +8 +4	77 <b>Ir</b> +4 +3	78 <b>Pt</b> +4 +2	79 <b>Au</b> +3 +1	80 <b>Hg</b> +2 +1	81 <b>TI</b> +3 +1	82 <b>Pb</b> +4 +2	83 <b>Bi</b> +5 +3	84 <b>Po</b> +2	85 At -1	86 <b>Rn</b>

**Combination Reaction** 

 $A + B \rightarrow C$   $2 \stackrel{0}{\text{Al}} + 3 \stackrel{0}{\text{Br}}_2 \rightarrow 2 \stackrel{+3}{\text{Al}} \stackrel{-1}{\text{Br}}_3$ 



#### **Decomposition Reaction**



 $C \rightarrow A + B$ 

 $2 \overset{+1}{\mathrm{K}} \overset{+5}{\mathrm{Cl}} \overset{-2}{\mathrm{O}_{3}} \rightarrow 2 \overset{+1}{\mathrm{K}} \overset{-1}{\mathrm{Cl}} + 3 \overset{0}{\mathrm{O}_{2}}$ 

**Combustion Reaction** 

$$A + O_2 \rightarrow B$$
  
$$\overset{0}{S} + \overset{0}{O}_2 \rightarrow \overset{+4}{S} \overset{-2}{O}_2$$



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

**Displacement Reaction** 

$$A + BC \rightarrow AC + B$$

 $\int_{Sr}^{0} + 2 H_{2} O \rightarrow Sr(OH)_{2} + H_{2} O$   $+4 Ti Cl_{4} + 2 Mg \rightarrow Ti + 2 Mg Cl_{2} OI_{2} OI_{$ 

Hydrogen Displacement

Metal Displacement

Halogen Displacement

#### The Activity Series for Metals

#### Hydrogen Displacement Reaction

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

 $M + BC \rightarrow MC + B$ 

M is metal BC is acid or  $H_2O$ B is  $H_2$ 

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

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

**Reducing strength increases** 

### The Activity Series for Halogens

 $F_2 > Cl_2 > Br_2 > I_2$ 



#### Halogen Displacement Reaction

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

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

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#### **Disproportionation Reaction**

The same element is simultaneously oxidized and reduced.

Example: reduced  $Cl_2 + 20H^- \rightarrow Cl0^- + Cl^- + H_20$ oxidized

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)  $6\text{Li}(s) + \text{N}_2(g) \longrightarrow 2\text{Li}_3\text{N}(s)$ 

(c)  $\operatorname{Ni}(s) + \operatorname{Pb}(\operatorname{NO}_3)_2(aq) \longrightarrow \operatorname{Pb}(s) + \operatorname{Ni}(\operatorname{NO}_3)_2(aq)$ 

(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<sub>2</sub> and it is +3 in HNO<sub>2</sub> and +5 in HNO<sub>3</sub>. Because the oxidation number of the *same* element both increases and decreases, this is a disproportionation reaction.

#### Chemistry in Action: Breath Analyzer

#### $3CH_{3}CH_{2}OH + 2K_{2}Cr_{2}O_{7} + 8H_{2}SO_{4} \rightarrow 3CH_{3}COOH + 2Cr_{2}(SO_{4})_{3} + 2K_{2}SO_{4} + 11H_{2}O$



### Solution Stoichiometry

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

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

# Preparing a Solution of Known Concentration



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

moles of solute = molarity  $\times$  L soln

Thus,

moles of 
$$K_2Cr_2O_7 = \frac{2.16 \text{ mol } K_2Cr_2O_7}{1 \text{ L-sofn}} \times 0.250 \text{ L-sofn}$$
  
= 0.540 mol  $K_2Cr_2O_7$ 

The molar mass of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is 294.2 g, so we write

grams of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> needed = 0.540 mol K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> × 
$$\frac{294.2 \text{ g K}_2\text{Cr}_2\text{O}_7}{1 \text{ mol K}_2\text{Cr}_2\text{O}_7}$$
  
= 159 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

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

$$3.81 \text{ g } C_6 H_{12} O_6 \times \frac{1 \text{ mol } C_6 H_{12} O_6}{180.2 \text{ g } C_6 H_{12} O_6} = 2.114 \times 10^{-2} \text{ mol } C_6 H_{12} O_6$$

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

$$V = \frac{n}{M}$$
  
=  $\frac{2.114 \times 10^{-2} \text{ mol } C_6 H_{12} O_6}{2.53 \text{ mol } C_6 H_{12} O_6 / L \text{ soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}}$   
= 8.36 mL soln

# Dilution

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



Describe how you would prepare  $5.00 \times 10^2$  mL of a 1.75 *M* H<sub>2</sub>SO<sub>4</sub> solution, starting with an 8.61 *M* stock solution of H<sub>2</sub>SO<sub>4</sub>.

**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:

$M_{\rm i} = 8.61$	M	$M_{\rm f} =$	1.75	М	
$V_{\rm i} = ?$		$V_{\rm f} =$	5.00	$\times$	$10^2 \mathrm{mL}$

Substituting in Equation (4.3),

$$8.61 \ M)(V_{\rm i}) = (1.75 \ M)(5.00 \times 10^{2} \ {\rm mL})$$
$$V_{\rm i} = \frac{(1.75 \ M)(5.00 \times 10^{2} \ {\rm mL})}{8.61 \ M}$$
$$= 102 \ {\rm mL}$$

Thus, we must dilute 102 mL of the 8.61 M H<sub>2</sub>SO<sub>4</sub> solution with sufficient water to give a final volume of  $5.00 \times 10^2$  mL in a 500-mL volumetric flask to obtain the desired concentration.

### Gravimetric Analysis

- 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







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<sub>3</sub>. 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

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

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

mass of Cl = 
$$0.2472 \times 1.0882$$
 g  
=  $0.2690$  g

Because the original compound also contained this amount of Cl<sup>-</sup> ions, the percent by mass of Cl in the compound is

$$\% \text{Cl} = \frac{0.2690 \text{ g}}{0.5662 \text{ g}} \times 100\%$$
$$= 47.51\%$$

### Titrations 1

In a *titration,* a solution of accurately known concentration 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 color at (or near) the equivalence point



Slowly add base to unknown acid UNTIL the indicator changes color



### Titrations 2

Titrations can be used in the analysis of: Acid-base reactions  $H_2SO_4 + 2NaOH \rightarrow 2H_2O + Na_2SO_4$ 



**Redox reactions** 

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

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:

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

Because 1 mol KHP  $\simeq$  1 mol NaOH, there must be 2.678  $\times$  10<sup>-3</sup> 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:

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

How many milliliters (mL) of a 0.610 M NaOH solution are needed to neutralize 20.0 mL of a 0.245 M H<sub>2</sub>SO<sub>4</sub> solution?

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

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

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

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

or

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

A 16.42-mL volume of 0.1327 M KMnO<sub>4</sub> solution is needed to oxidize 25.00 mL of a FeSO<sub>4</sub> solution in an acidic medium. What is the concentration of the FeSO<sub>4</sub> 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

moles of KMnO<sub>4</sub> = 
$$\frac{0.1327 \text{ mol KMnO}_4}{1000 \text{ mL soln}} \times 16.42 \text{ mL}$$
  
=  $2.179 \times 10^{-3} \text{ mol KMnO}_4$ 

From the net ionic equation we see that 5 mol  $\text{Fe}^{2+} \simeq 1 \text{ mol } \text{MnO}_4^-$ . Therefore, the number of moles of FeSO<sub>4</sub> oxidized is

moles 
$$\text{FeSO}_4 = 2.179 \times 10^{-3} \text{ mol KMnO}_4 \times \frac{5 \text{ mol FeSO}_4}{1 \text{ mol KMnO}_4}$$
  
= 1.090 × 10<sup>-2</sup> mol FeSO<sub>4</sub>

The concentration of the FeSO<sub>4</sub> solution in moles of FeSO<sub>4</sub> per liter of solution is

molarity of FeSO<sub>4</sub> = 
$$\frac{\text{mol FeSO}_4}{\text{L soln}}$$
  
=  $\frac{1.090 \times 10^{-2} \text{ mol FeSO}_4}{25.00 \text{ mL soln}} \times \frac{1000 \text{ mL soln}}{1 \text{ L soln}}$   
= 0.4360 M

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