

Reactions in Aqueous Solution

Chapter 4



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

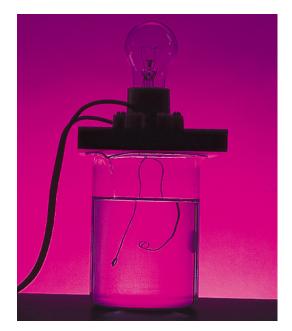
Solution	Solvent	<u>Solute</u>
Soft drink (l)	H_2O	Sugar, CO ₂
Air (g)	N_2	O ₂ , Ar, CH ₄
Soft Solder (s)	Pb	Sn



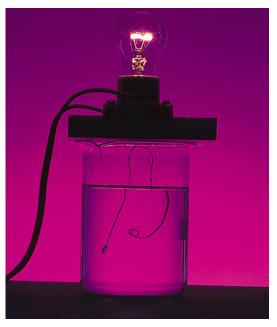
aqueous solutions of KMnO₄

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

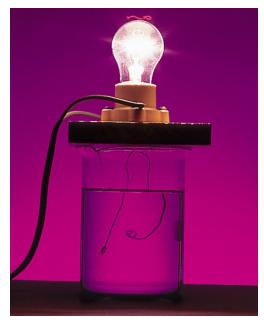
A *nonelectrolyte* is a substance that, when dissolved, results in a solution that does not conduct electricity.



nonelectrolyte



weak electrolyte



strong electrolyte

Conduct electricity in solution?

Cations (+) and Anions (-)

Strong Electrolyte – 100% dissociation

NaCl (s)
$$\xrightarrow{\text{H}_2\text{O}}$$
 Na⁺ (aq) + Cl⁻ (aq)

Weak Electrolyte – not completely dissociated

$$CH_3COO+ \longrightarrow CH_3COO-(aq) + H^+(aq)$$

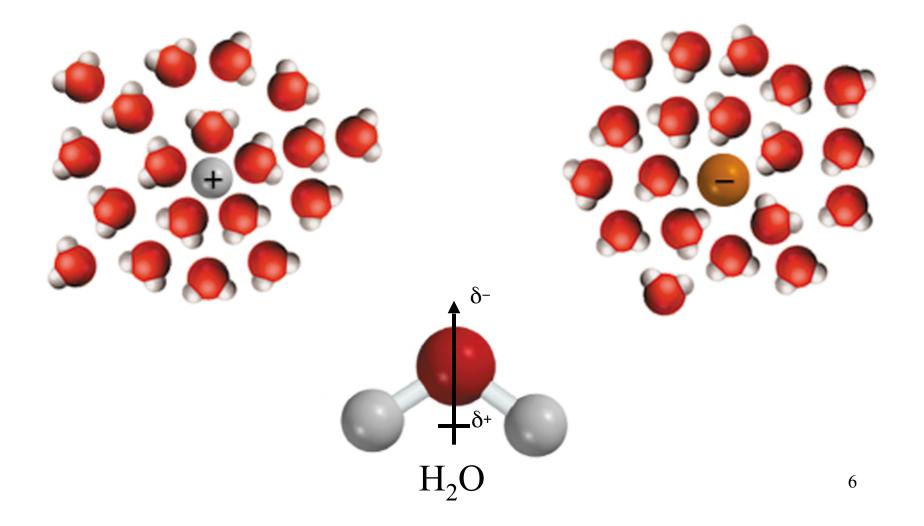
Ionization of acetic acid

CH₃COOH
$$\bigcirc$$
 CH₃COO- (aq) + 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 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

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

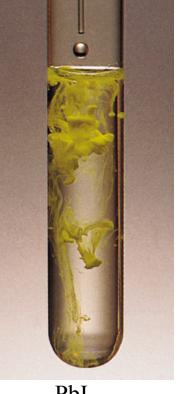
TABLE 4.1	LE 4.1 Classification of Solutes in Aqueous Solution							
Strong Ele	ctrolyte	Weak Electrolyte	Nonelectrolyte					
HC1		CH ₃ COOH	(NH ₂) ₂ CO (urea)					
HNO_3		HF	CH ₃ OH (methanol)					
$HClO_4$		HNO_2	C ₂ H ₅ OH (ethanol)					
H_2SO_4*		NH_3	C ₆ H ₁₂ O ₆ (glucose)					
NaOH		$ m H_2O^\dagger$	$C_{12}H_{22}O_{11}$ (sucrose)					
Ba(OH) ₂								
Ionic compo	ounds							

^{*}H₂SO₄ has two ionizable H⁺ ions.

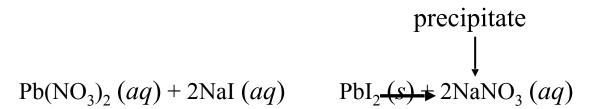
[†]Pure water is an extremely weak electrolyte.

Precipitation Reactions

Precipitate – insoluble solid that separates from solution



 PbI_2



molecular equation

$$Pb^{2+} + 2NO_3^- + 2Na^+ + 2I^ PbI_2(s) + 2Na^+ + 2NO_3^-$$

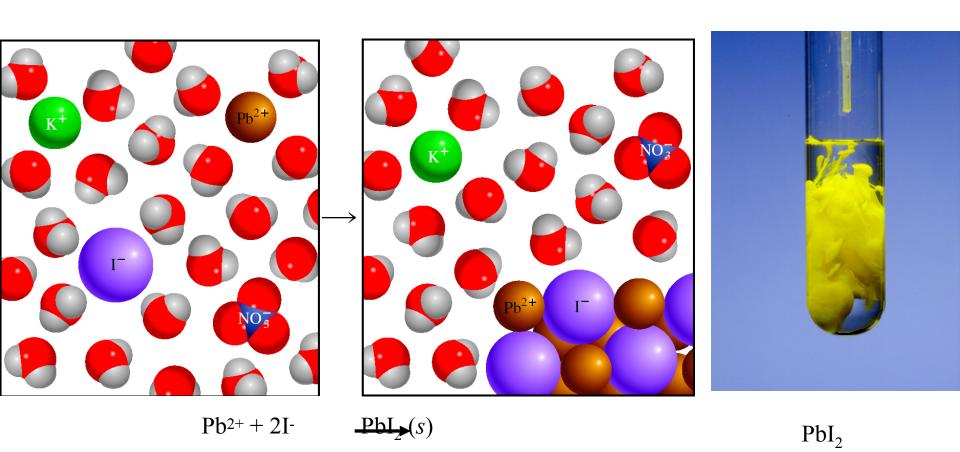
ionic equation

$$Pb^{2+} + 2I$$
 PbI (s)

net ionic equation

Na⁺ and NO₃⁻ are *spectator* ions

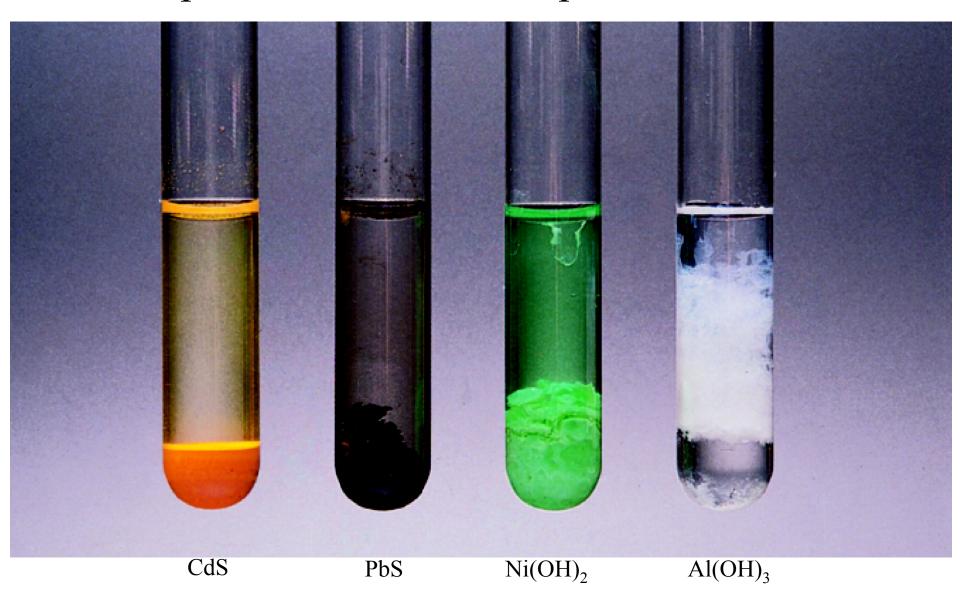
Precipitation of Lead Iodide



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 ⁻), bicarbonates (HCO ₃ ⁻), and chlorates (ClO ₃ ⁻)							
Halides (Cl ⁻ , Br ⁻ , I ⁻)	Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}						
Sulfates (SO ₄ ²⁻)	Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}						
Insoluble Compounds	Soluble Exceptions						
Carbonates (CO_3^{2-}) , phosphates (PO_4^{3-}) , chromates (CrO_4^{2-}) , sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion						
Hydroxides (OH ⁻)	Compounds containing alkali metal ions and the Ba ²⁺ ion						

Examples of Insoluble Compounds



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

Write the net ionic equation for the reaction of silver nitrate with sodium chloride.

$$AgNO_{3}(aq) + NaCl(aq)$$
 ____AgCl(s) + NaNO₃(aq)
 $Ag^{+} + NO_{3}^{-} + Na^{+} + Cl^{-}$ ___AgCl(s) + Na++NO₃-

$$Ag^+ + Cl^- \longrightarrow AgCl(s)$$

Chemistry In Action:

An Undesirable Precipitation Reaction

$$Ca^{2+}(aq) + 2HCO_3(aq)$$
 - $CaCO_3(aq) + CO_2(aq) + H_2O(l)$
 $CO_2(aq)$ - $CO_2(aq)$

Boiler Scale Deposits



Properties of Acids

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

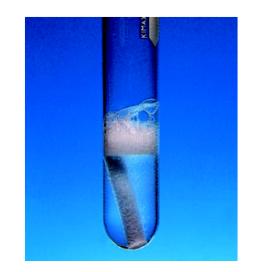
Cause color changes in plant dyes.

React with certain metals to produce hydrogen gas.

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

React with carbonates and bicarbonates to produce carbon dioxide gas

2HCl
$$(aq)$$
 + CaCO₃ (s) CaCl₂ (aq) \neq CO₂ (g) + H₂O (l)



Aqueous acid solutions conduct electricity.

Properties of Bases

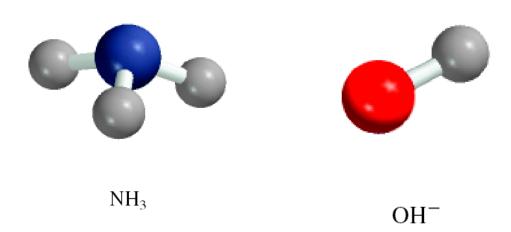
Have a bitter taste.

Feel slippery. Many soaps contain bases.

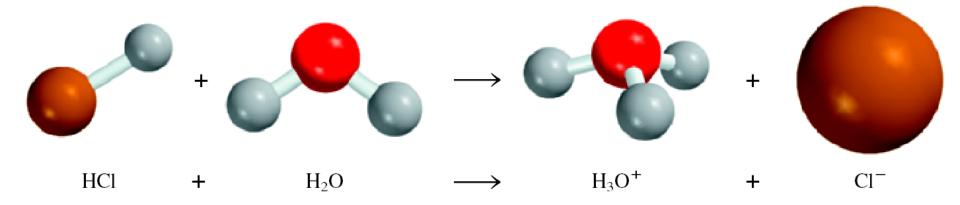
Cause color changes in plant dyes.

Aqueous base solutions conduct electricity.

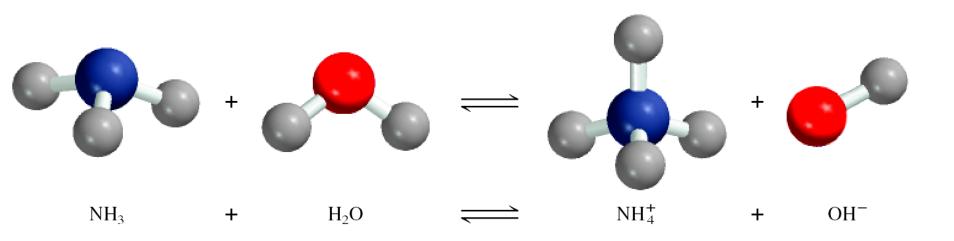
Examples:



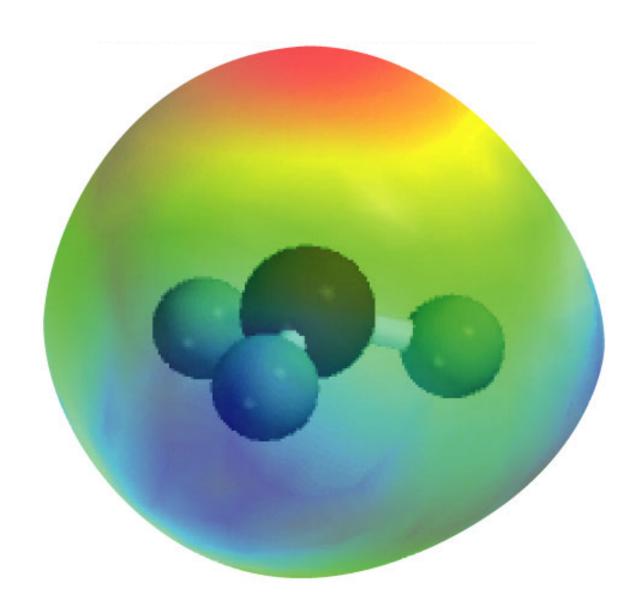
Arrhenius acid is a substance that produces $H^+(H_3O^+)$ in water



Arrhenius base is a substance that produces OH- in water

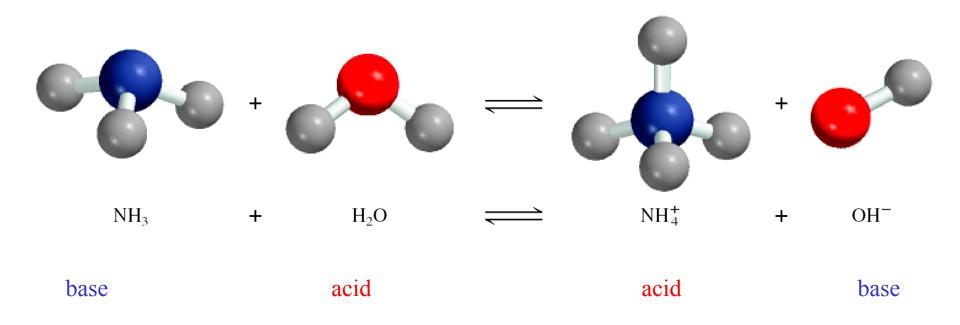


Hydronium ion, hydrated proton, H₃O⁺



A Brønsted acid is a proton donor

A Brønsted base is a proton acceptor



A Brønsted acid must contain at least one ionizable proton!

Monoprotic acids

$$HC1$$
 $H^+ + C1$

$$HNO_3$$
 $H + NO_3$

$$CH_3COOH$$
 $\underline{H^{++}}CH_3COO^{-}$

Diprotic acids

$$H_2SO_4$$
 H_2^+ $+$ HSO_4^-

$$HSO_4$$
 $H^{\pm} + SO_4^2$

Strong electrolyte, strong acid

Weak electrolyte, weak acid

Triprotic acids

$$H_3PO_4$$
 $H^{\pm} + H_2PO_4$

$$H_2PO_4$$
 \longrightarrow HPO_4^2 -

$$HPO_4^{2-}$$
 $H^+ + PO_4^{3-}$

Weak electrolyte, weak acid

Weak electrolyte, weak acid

Weak electrolyte, weak acid

TABLE 4.3

Some Common Strong and Weak Acids

Strong Acids

Hydrochloric HCl

acid

Hydrobromic

HBr

HI

acid

Hydroiodic

acid

Nitric acid

 HNO_3

Sulfuric acid

 H_2SO_4

Perchloric acid

 $HClO_4$

Weak Acids

Hydrofluoric

HF

acid

Nitrous acid

 HNO_2

Phosphoric acid

 H_3PO_4

Acetic acid

CH₃COOH

Identify each of the following species as a Brønsted acid, base, or both. (a) HI, (b) CH_3COO^- , (c) $H_2PO_4^-$

$$HI(aq)$$
 $H+(aq)+I-(aq)$

Brønsted acid

$$CH_3COO^-(aq) + H^+(aq)$$
 $CH_3CQOH(aq)$

Brønsted base

$$H_2PO_4^-(aq)$$
 $H_4^+(aq) + HPO_4^{2-}(aq)$

Brønsted acid

$$H_2PO_4^-(aq) + H^+(aq) \qquad H_3PO_{4}(aq)$$

Brønsted base

Neutralization Reaction

HCl
$$(aq)$$
 + NaOH (aq) — NaCl (aq) + H₂O
H+ + Cl- + Na+ + OH- — Na+ + Cl- + H₂O
H+ + OH- — H₂O

Neutralization Reaction Involving a Weak Electrolyte

HCN
$$(aq)$$
 + NaOH (aq) —NaCN (aq) + H₂O
HCN + Na+ OH- —Na+ CN- + H₂O
HCN + OH- —CN- + H₂O

Neutralization Reaction Producing a Gas

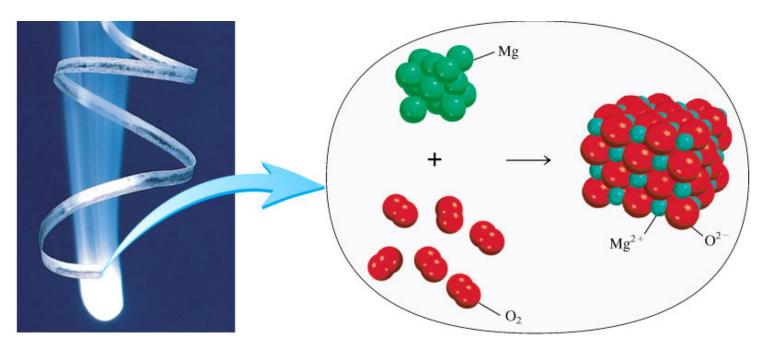
$$\frac{\text{acid} + \text{base}}{\text{acid}} = \frac{\text{salt} + \text{water} + \text{CO}_2}{\text{salt}}$$

$$\frac{2HCl}{(aq) + Na_2CO_3}(aq) - \frac{2}{NaCl}(aq) + H_2O + CO_2$$

$$2H^{+} + 2Cl^{-} + 2Na^{+} + CO_{3}^{2-}$$
 $-2Na^{+} + 2Cl^{-} + H_{2}O + CO_{2}$
 $2H^{+} + CO_{3}^{2-}$ $-H_{2}O + CO_{2}$

Oxidation-Reduction Reactions

(electron transfer reactions)



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

Oxidation half-reaction (lose e-)

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

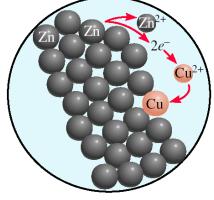
Reduction half-reaction (gain e-)

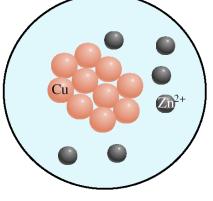
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$$2Mg + O_2 + 4e$$
 $-2Mg^{2+} + 2O^{2-} + 4e$ $-2MgO$

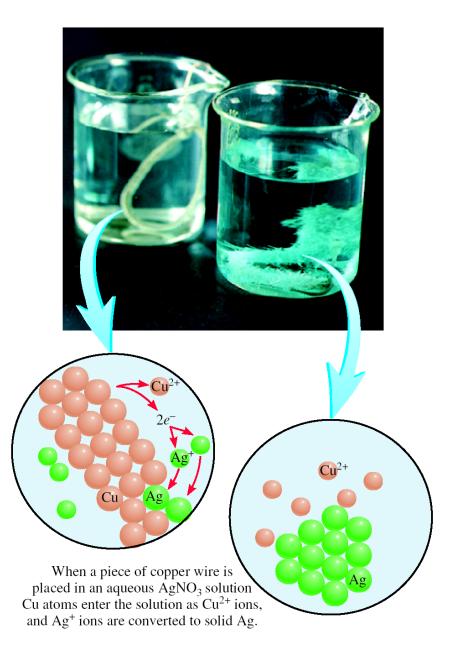


The Zn bar is in aqueous solution of CuSO₄





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



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

$$Zn = Zn^{2+} + 2e^{-}$$

Zn is oxidized

Zn is the *reducing agent*

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



Cu²⁺ is reduced

Cu²⁺ is the *oxidizing agent*

Copper wire reacts with silver nitrate to form silver metal. What is the oxidizing agent in the reaction?

$$\operatorname{Cu}(s) + 2\operatorname{AgNO}_3(aq) \qquad -\operatorname{Cu}(\operatorname{NO}_3)_2(aq) + 2\operatorname{Ag}(s)$$

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

$$Ag^+ + 1e^ Ag^-$$

Ag⁺ is reduced

Ag⁺ is the oxidizing agent

Oxidation number

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_2O_2 and O_2^2 it is -1.

- 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. Oxidation number of oxygen in the superoxide ion, O_2^- , is $-\frac{1}{2}$.

$$HCO_3^ O = -2$$
 $H = +1$
 $3x(-2) + 1 + ? = -1$
 $C = +4$

The Oxidation Numbers of Elements in their Compounds

1 1A																	18 8A
1 H +1 -1																	2 He
	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	
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 -1 -1 -2	9 F -1	10 Ne
11 Na +1	12 Mg +2	3	4	5	6	7	8	9	10	11	12	13 Al +3	14 Si +4 -4	15 P +5 +3 -3	16 S +6 +4 +2 -2	17 CI +7 +6 +5 +44 +1	18 Ar
10	20	3B	4B	5B	6B	7B		-8B-		1B	2B	24	22	22			26
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

What are the oxidation numbers of all the elements in each of these compounds?

$$NaIO_3$$
 \overline{IF}_7 $K_2Cr_2O_7$

$$F = -1$$

$$7x(-1) + ? = 0$$

$$I = +7$$

$$Na = +1 O = -2$$

$$3x(-2) + 1 + ? = 0$$

$$I = +5$$

$$O = -2$$
 $K = +1$

$$7x(-2) + 2x(+1) + 2x(?) = 0$$

$$Cr = +6$$

Types of Oxidation-Reduction Reactions

Combination Reaction

$$A + B \longrightarrow C$$

$${}^{0} {}^{0} {}^{0} {}^{+3} {}^{-1}$$

$$2A1 + 3Br_{2} \longrightarrow 2A1Br_{3}$$



Decomposition Reaction



$$C \longrightarrow A + B$$

$${^{+1}}_{2KClO_3}^{+1} \longrightarrow {^{+1}}_{2KCl}^{-1} + {^{1}}_{3O_2}^{0}$$

Types of Oxidation-Reduction Reactions

Combustion Reaction

$$A + O_2 \longrightarrow B$$

$$\overset{0}{S} + \overset{0}{O_2} \longrightarrow \overset{+4}{S} \overset{-2}{O_2}$$





$$0 0 +2 -2$$

 $2Mg + O_2 \longrightarrow 2MgO$

Types of Oxidation-Reduction Reactions

Displacement Reaction

$$A + BC \longrightarrow AC + B$$

$$Sr + 2H_2O \longrightarrow Sr(OH)_2 + H_2^0$$
 Hydrogen Displacement

$$TiCl_4 + 2Mg$$
 $\longrightarrow Ti + 2MgCl_2$ Metal Displacement

$$Cl_2 + 2KBr \longrightarrow 2KCl + Br_2$$
 Halogen Displacement

The Activity Series for Metals

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

Hydrogen Displacement Reaction

$$M + BC \longrightarrow MC + B$$

M is metal

BC is acid or H₂O B is H₂

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

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

The Activity Series for Halogens

$$F_2 > Cl_2 > Br_2 > I_2$$



Halogen Displacement Reaction

$$\overset{0}{\text{Cl}_2} + 2\text{KBr} \longrightarrow 2\text{KCl} + \text{Br}_2$$

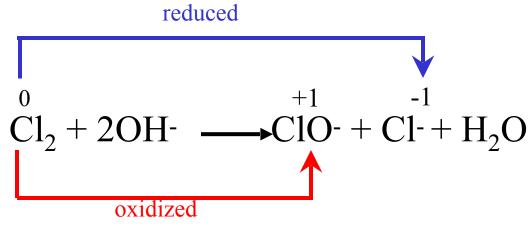
$$I_2 + 2KBr - 2KI + Br_2$$

Types of Oxidation-Reduction Reactions

Disproportionation Reaction

The same element is simultaneously oxidized and reduced.

Example:



Classify each of the following reactions.

$$Ca^{2+} + CO_3^{2-}$$
 —Ca CO_3

Precipitation

$$NH_3 + H^+ \longrightarrow NH_4^+$$

Acid-Base

$$Zn + 2HC1 \longrightarrow ZnCl_2 + H_2$$

Redox (H₂ Displacement)

$$Ca + F_2 \longrightarrow CaF_2$$

Redox (Combination)

Chemistry in Action: Breath Analyzer

$$+6$$

$$3CH3CH2OH + 2K2Cr2O7 + 8H2SO4$$

$$+3$$
 $3CH_3COOH + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$



Solution Stoichiometry

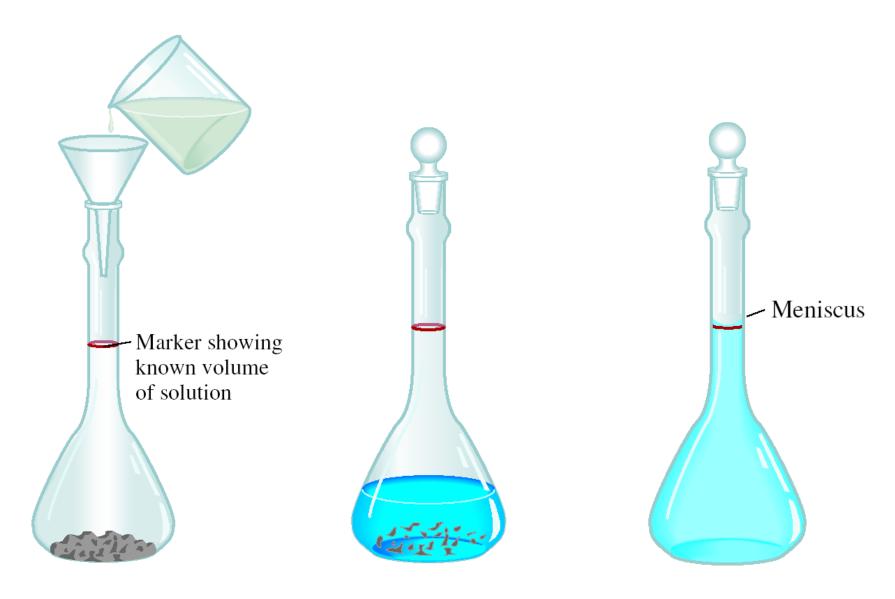
The *concentration* of a solution is the amount of solute present in a given quantity of solvent or solution.

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

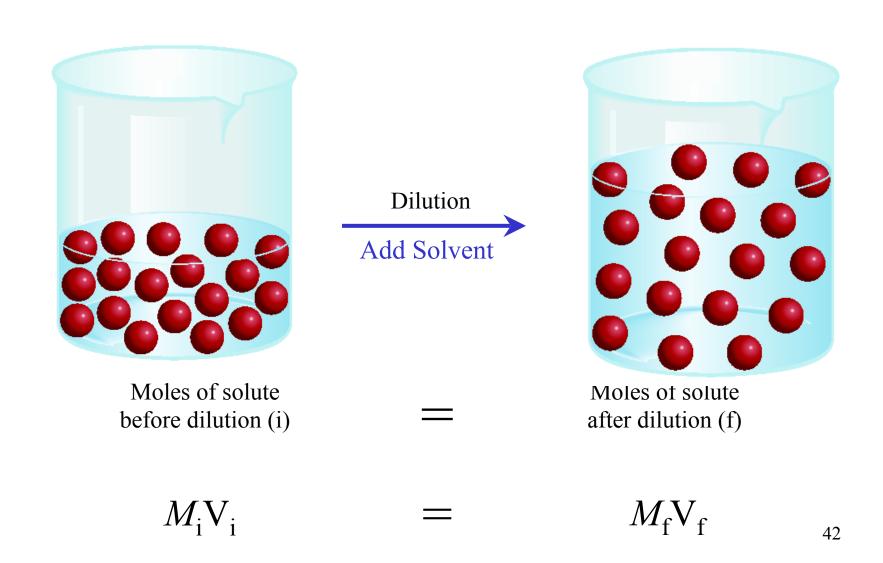
What mass of KI is required to make 500. mL of a 2.80 *M* KI solution?

volume of KI solution
$$\xrightarrow{M \text{ KI}}$$
 moles KI $\xrightarrow{M \text{ KI}}$ grams KI
500. mL x $\frac{1 \text{ L}}{1000 \text{ mL}}$ x $\frac{2.80 \text{ mol KI}}{1 \text{ Lsoln}}$ x $\frac{166 \text{ g KI}}{1 \text{ mol KI}}$ = 232 g KI

Preparing a Solution of Known Concentration



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



How would you prepare 60.0 mL of 0.200 M HNO₃ from a stock solution of 4.00 M HNO₃?

$$M_{\rm i}V_{\rm i} = M_{\rm f}V_{\rm f}$$

$$M_{\rm i} = 4.00 \, M$$
 $M_{\rm f} = 0.200 \, M$ $V_{\rm f} = 0.0600 \, L$ $V_{\rm i} = ? \, L$

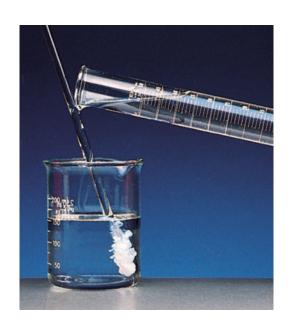
$$V_{i} = \frac{M_{f}V_{f}0.200 M \times 0.0600 L}{M_{i}} = 0.00300 L = 3.00 mL$$

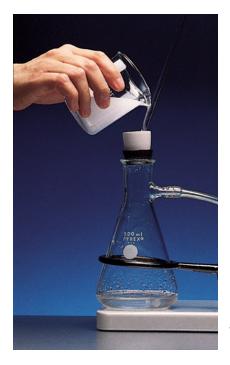
Dilute 3.00 mL of acid with water to a total volume of 60.0 mL.

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





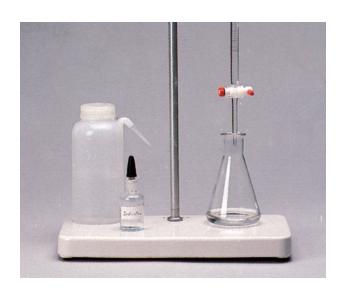


Titrations

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.

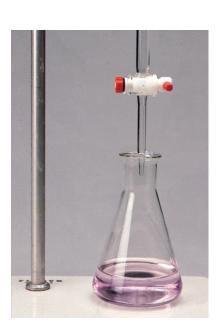
Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point



Slowly add base to unknown acid UNTIL

the indicator changes color



Titrations can be used in the analysis of

Acid-base reactions

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



Redox reactions



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

What volume of a 1.420 M NaOH solution is required to titrate 25.00 mL of a 4.50 M H₂SO₄ solution?

WRITE THE CHEMICAL EQUATION!

$$25.00 \text{ mL x} \frac{4.50 \text{ mol H}_2\text{SO}_4}{1000 \text{ mL soln}} \quad \text{x} \frac{2 \text{ mol NaOH}}{1 \text{ mol H}_2\text{SO}_4} \quad \text{x} \frac{1000 \text{ ml soln}}{1.420 \text{ mol NaOH}} = 158 \text{ mL}$$

16.42 mL of 0.1327 M KMnO₄ solution is needed to oxidize 25.00 mL of an acidic FeSO₄ solution. What is the molarity of the iron solution?

WRITE THE CHEMICAL EQUATION!

$$5Fe^{2+} + MnO_4^{-} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
volume red \xrightarrow{M} moles red \xrightarrow{rxn} moles oxid \xrightarrow{V} \xrightarrow{M} oxid \xrightarrow{red} moles oxid \xrightarrow{oxid}

$$16.42 \text{ mL} = 0.01642 \text{ L}$$

$$25.00 \text{ mL} = 0.02500 \text{ L}$$

$$0.01642 \text{ L} \times \frac{0.1327 \text{ mol KMnO}_4}{1 \text{ L}} \times \frac{5 \text{ mol Fe}^{2+}}{1 \text{ mol KMnO}_4} \times \frac{1}{0.02500 \text{ L Fe}^{2+}} = 0.4358 M$$

Chemistry in Action: Metals from the Sea

$$CaCO_3(s)$$
 $CaO(s) + CO_2(g)$

CaO (s) + H₂O (l)
$$- ea^{2+} (aq) + 2OH (aq)$$

$$Mg^{2+}(aq) + 2OH (aq) \longrightarrow Mg(OH)_2(s)$$

$$Mg(OH)_2(s) + 2HCl(aq)$$
 $\longrightarrow MgCl_2(aq) + 2H_2O(l)$

Magnesium Hydroxide

