Some Types of Reactions in Aqueous Solution
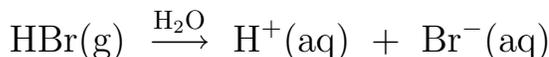
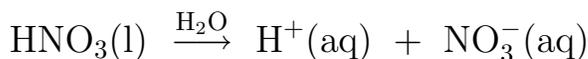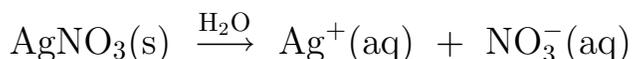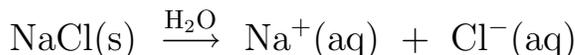## Electrolyte vs. Non-Electrolyte Solutions

An *aqueous* solution, is one in which water is the *solvent.*

When substances dissolve in solution, they may do so as whole, independent, uncharged molecules, or they may ionize. Since water molecules are "polar", they can orient themselves around atomic or molecular ions, stabilizing them so that the +'ve and −'ve ions are not energetically drawn together to recombining as neutral species.
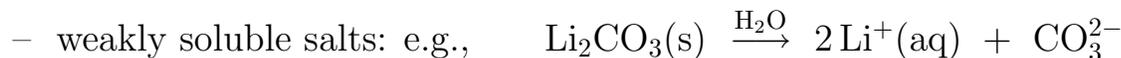
An ***electrolyte*** is a substance which ionizes when dissolved in water, yielding aqueous ions which can conduct electricity.

e.g., $NaCl(s)$, $MgBr_2(s)$, $HCl(g)$, $H_2SO_4(l)$, $NH_3(g)$, $AgNO_3(s)$

- A *strong electrolyte* is a substance which is essentially completely ionized in solution, making the resulting solution is a good conductor of electricity. Includes essentially all soluble ionic solids, as well as some molecular liquids and gases.

$$NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$$
$$AgNO_3(s) \xrightarrow{H_2O} Ag^+(aq) + NO_3^-(aq)$$
$$K_2SO_4(s) \xrightarrow{H_2O} 2K^+(aq) + SO_4^{2-}(aq)$$
$$HNO_3(l) \xrightarrow{H_2O} H^+(aq) + NO_3^-(aq)$$
$$HBr(g) \xrightarrow{H_2O} H^+(aq) + Br^-(aq)$$

- A *weak electrolyte* is a substance which is only slightly ionized in water – so the resulting solution is only a fair to poor conductor of electricity. This includes

  – weakly soluble salts: e.g., $\quad Li_2CO_3(s) \xrightarrow{H_2O} 2Li^+(aq) + CO_3^{2-}$

  – soluble molecular species which only partially ionize, such as all weak acids
  $$CH_3COOH(aq) \rightleftarrows H^+(aq) + CH_3COO^-(aq)$$

– soluble gases such as NH_3 and HF : $\qquad HF(aq) \xrightarrow{H_2O} H^+(aq) + F^-(aq)$

- A *non-electrolyte* is a substance which dissolves in water, but does not ionize, so the resulting solution does not conduct electric current.

  e.g., sugars (glucose, sucrose, ... etc.), methanol $CH_3OH(l) \xrightarrow{H_2O} CH_3OH(aq)$

Most solvated ions are polyatomic ions: either $+'$vely charged *cations* or $-'vely$ *charged* anions *, and you must learn to recognize and name these 'groups'.*

TABLE 3.3 Some Common Polyatomic Ions		
Name	Formula	Typical
Cation		
Ammonium ion	NH_4^+	NH_4Cl
Anions		
Acetate ion	$C_2H_3O_2^-$	$NaC_2H_3O_2$
Carbonate ion	CO_3^{2-}	Na_2CO_3
Hydrogen carbonate ion[a] (or bicarbonate ion)	HCO_3^-	$NaHCO_3$
Hypochlorite ion	ClO^-	$NaClO$
Chlorite ion	ClO_2^-	$NaClO_2$
Chlorate ion	ClO_3^-	$NaClO_3$
Perchlorate ion	ClO_4^-	$NaClO_4$
Chromate ion	CrO_4^{2-}	Na_2CrO_4
Dichromate ion	$Cr_2O_7^{2-}$	$Na_2Cr_2O_7$
Cyanide ion	CN^-	$NaCN$
Hydroxide ion	OH^-	$NaOH$
Nitrite ion	NO_2^-	$NaNO_2$
Nitrate ion	NO_3^-	$NaNO_3$
Oxalate ion	$C_2O_4^{2-}$	$Na_2C_2O_4$
Permanganate ion	MnO_4^-	$NaMnO_4$
Phosphate ion	PO_4^{3-}	Na_3PO_4
Hydrogen phosphate ion[a]	HPO_4^{2-}	Na_2HPO_4
Dihydrogen phosphate ion[a]	$H_2PO_4^-$	NaH_2PO_4
Sulfite ion	SO_3^{2-}	Na_2SO_3
Hydrogen sulfite ion[a] (or bisulfite ion)	HSO_3^-	$NaHSO_3$
Sulfate ion	SO_4^{2-}	Na_2SO_4
Hydrogen sulfate ion[a] (or bisulfate ion)	HSO_4^-	$NaHSO_4$
Thiosulfate ion	$S_2O_3^{2-}$	$Na_2S_2O_3$

[a] These anion names are sometimes written as a single word—for example, hydrogencarbonate, hydrogenphosphate, and so forth.

1. Precipitation Reactions

Some metal salts [a **salt** *is an ionic compound whose component ions* **do not** *include* H^+ or OH^-] are highly soluble and some are not. If the ions of a weakly soluble or *in*soluble salt meet in solution, they will form a solid precipitate and drop out of solution.

e.g., both $AgNO_3$ and K_2SO_4 are strong electrolytes, so that in separate aqueous solutions we have

$$AgNO_3(s) \xrightarrow{H_2O} Ag^+(aq) + NO_3^-(aq)$$

$$K_2SO_4(s) \xrightarrow{H_2O} 2K^+(aq) + SO_4^{2-}(aq)$$
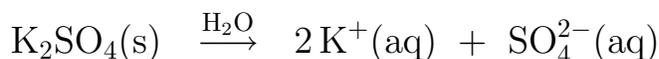
However, Ag_2SO_4 is a very weakly soluble salt, and if we mix together solutions of $AgNO_3$ and K_2SO_4 a solid $Ag_2SO_4(s)$ precipitate will spontaneously form which will remove most of the $Ag^+(aq)$ and/or $SO_4^{2-}(aq)$ from solution.

$$Ag^+(aq) + NO_3^-(aq) + K^+(aq) + SO_4^{2-}(aq)$$

$$\longrightarrow Ag_2SO_4(s) + K^+(aq) + NO_3^-(aq)$$
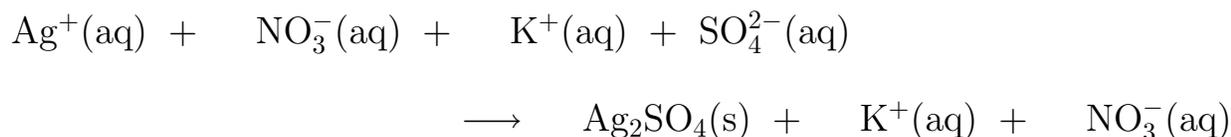
Usually write only the *"net ionic equation"* which neglects the "spectator ions".

Exercise 1. Given that $Ag_2SO_4(s)$ is a (fairly) insoluble salt, what are the final molar concentrations of the various species present in solution obtained after on mixing 255 mL of $0.555\,M$ $AgNO_3$ solution with $365\,mL$ of $0.250\,M$ K_2SO_4 solution?

What substances tend to be soluble (and hence do *not* form precipitates)?

- all compounds formed from the Group-1 alkali metals (Li, Na, K, Rb, Cs, Fr)

- all salts formed from the ammonium ion NH_4^+

- all nitrates (i.e., salts formed with NO_3^-), perchlorates (formed from ClO_4^-) and acetates (formed from $CH_3CO_2^-$)

- all chlorides (Cl^-), bromides (Br^-) & iodides (I^-) *except for* their salts with silver (Ag^+), lead (Pb^{2+}) and mercury (Hg^+ and Hg_2^{2+}).

- most sulphates (SO_4^{2-}), except for those formed with heavy group II metals (Ca^{2+}, Sr^{2+}, Ba^{2+}) and with Ag^+, Pb^{2+} and Hg_2^{2+}.
  { $CaSO_4$ is only slightly soluble.}

**What substances tend to be insoluble** (and hence *do* form precipitates)?

- hydroxides (containing OH^-), *except for* those formed with alkali (group 1) metals and NH_4^+; hydroxides formed with group II metals Ca^{2+}, Sr^{2+} & Ba^{2+} are slightly soluble

- sulfides (formed from S^{2-}), *except for* those with the group-1 (alkali) and group-2 (alkaline earth: Be, Mg, Ca, ... etc.) metals and ammonium NH_4^+, which are soluble.

- carbonates (involving CO_3^{2-}), phosphates (PO_4^{3-}) and sulphites (SO_3^{2-}), *except for* those formed with alkali (group 1) metals and NH_4^+

Note that all the above rules apply to salts, which ionize when they dissolve.

However, we have *no analogous general rules for non-salts*

- they may or may not be soluble in water

- if soluble, they may or may not ionize

  e.g. — sugar ($C_{12}H_{22}O_{11}$) and ethanol (C_2H_5OH) are very soluble in water and do not ionize

  — HCl(g) is very soluble and is a very strong electrolyte

  — HF and acetic acid (CH_3COOH) are very soluble in water, but are "weak acids" with very limited tendency to ionize

What determines whether or not particular substances will or will not form precipitates ?
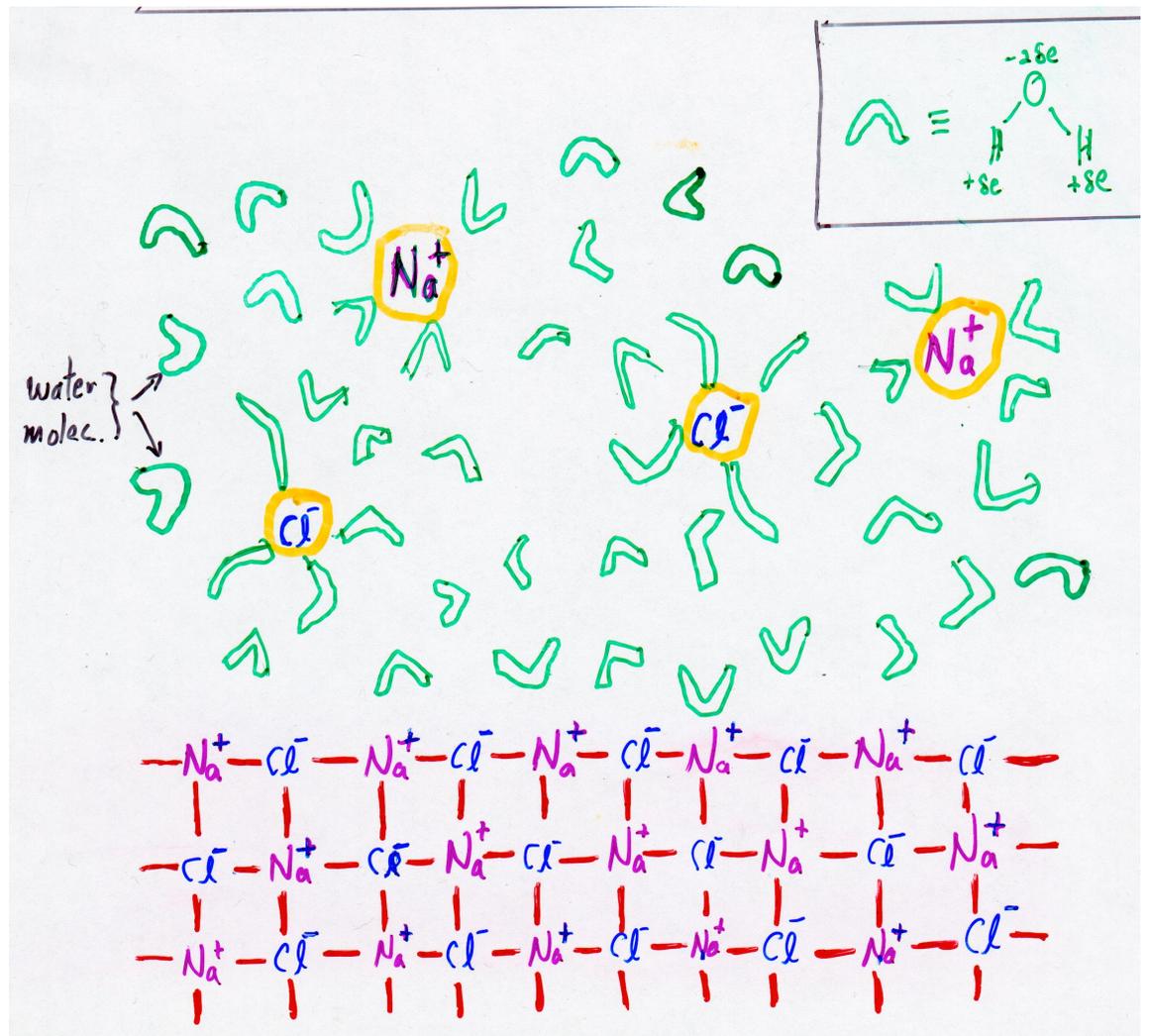
Exercise 2. If $300\,\text{mL}$ of a $0.544\,\text{M}$ solution of $\text{Bi(NO}_3)_3$ is added to $400\,\text{mL}$ of a $0.266\,\text{M}$ solution of K_2S:

    a) Does a reaction occur? If so, what happens?

    b) What is the net ionic equation for the reaction?

    c) What is the limiting reagent?

    d) What are the concentrations of aqueous solutes when the reaction is complete?

Exercise 3. For each of the following: (a) Does a reaction occur?
(b) If yes, write the net ionic equation.

$$Al_2(SO_4)_3\,(aq)\ +\ BaCl_2\,(aq)\ \longrightarrow\ \ ??$$

$$(NH_4)_2CO_3\,(aq)\ +\ Pb(NO_3)_2\,(aq)\ \longrightarrow\ \ ??$$
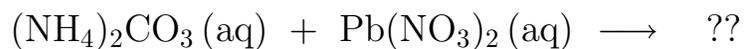
Exercise 4. Consider the precipitation reaction:

$$AgNO_3\,(aq) + NaCl\,(aq)\ \longrightarrow\ AgCl(s) + NaNO_3\,(aq)$$

(a) Write the net ionic equation.

If $350\,\mathrm{mL}$ of $1.30\,\mathrm{M}$ $AgNO_3\,(aq)$ solution are added to $250\,\mathrm{mL}$ of $2.40\,\mathrm{M}$ $NaCl\,(aq)$ solution:

(b) How many grams of $AgCl\,(s)$ are formed?

(c) What are the final concentrations of all species remaining in solution?

2. *Acids, Bases & Acid/Base Neutralization*

Chemists have a number of different ways of defining what is an *acid* and a *base*. Chapter 5 uses one definition (Arrhenius) & Chapts. 16 & 17 use another.

An **acid** is a substance which yields $H^+(aq)$ when dissolved in water [Arrhenius].

An **acid** is a species which donates a proton $H^+(aq)$ to some other species in solution [Brønsted-Lowrey].

Arrhenius says a *strong acid* is one which ionizes almost completely in water.

A *weak acid* is one which is only partially ionized in water.

A **base** is a substance which yields OH^-(aq) when dissolved in water. [Arrhenius]

An **base** is a species which accepts a proton $H^+(aq)$ [Brønsted-Lowrey]

Arrhenius says a *strong base* is one which ionizes almost completely in water.

A *weak base* is one which is only partially ionized or yields only small amounts of OH^-(aq) when dissolved in water.

Form of typical Arrhenius acid/base Neutralization Reactions:
An acid reacts with a base to form a "salt" and water. If either the acid or the base is "strong", the neutralization reaction goes (essentially: see Chapt. 17 & 18) to completion.

Often monitor the progress of an acid–base neutralization using a tiny amount of an "indicator", a substance which has one colour in an acidic solution and another colour if the solution is basic. If we slowly add an acid solution to a basic solution coloured by a small drop of indicator, the onset of the colour change indicates quantitative neutralization of the acid by the base (and vise versa).

| Strong Acids	Strong bases
HCl	LiOH
HBr	NaOH
HI	KOH
$HClO_4$	RbOH
HNO_3	CsOH
H_2SO_4	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Volumetric Analysis

A common problem in analytical chemistry is determining the concentration of an unknown solution. Often do this by titrating with a solution of known concentration.

e.g. We wish to determine the concentration of an uncalibrated $Ba(OH)_2$ solution.

Procedure:

1. Measure out a precisely known volume of the solution of unknown concentration (in this case, the base, $Ba(OH)_2$). For our example, assume we have $50.00\,mL$ of this basic solution.

2. Add a tiny amount of a chemical indicator which will change colour when the reaction is complete.

3. Titrate with a solution of some strong acid of precisely known concentration (say, with a $0.1234\,M$ solution of $HCl(aq)$) to find exactly what volume of acid must be added to achieve a colour change.

4. Calculate the concentration of the unknown (assuming the colour change occurs when $47.42\,mL$ of acid solution has been added).
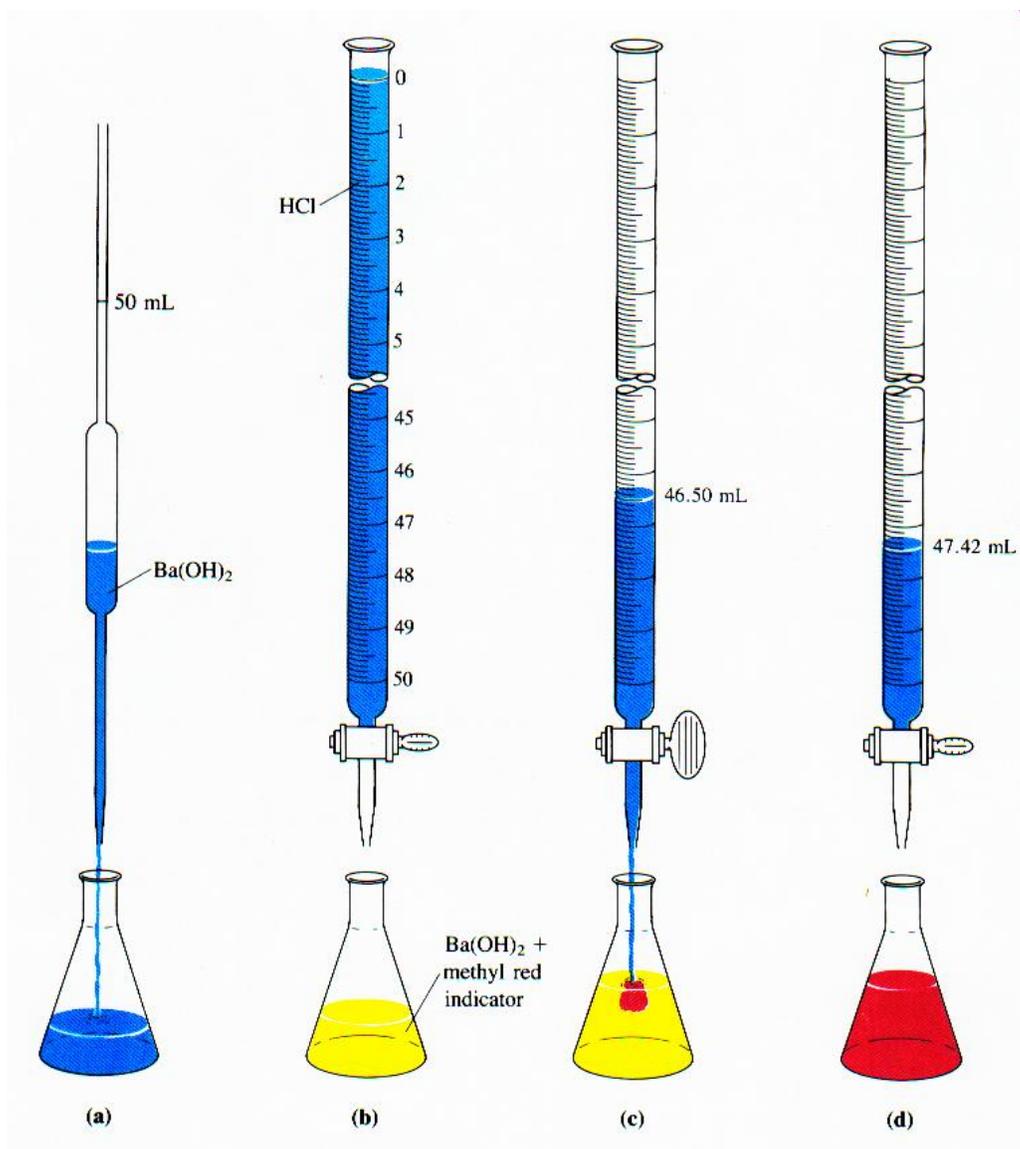
Solution: Begin by delineating precisely *what is happening?*
{write the overall and the net ionic equations}

For our neutralization reaction, we know the amount and concentration of acid, so:

{*amount reaction*} =

Exercise 5. What volume of a $0.234\,M$ solution of $Ba(OH)_2$ would be required to precisely neutralize $750.0\,mL$ of a $0.7532\,M$ solution of the weak acid $CH_3COO\text{-}H$?

Exercise 6. A $10.00\,mL$ sample of stock phosphoric acid solution $H_3PO_4\,(aq)$ is diluted to $50.00\,mL$, and then titrated with a known KOH solution. If $55.58\,mL$ of that $1.554\,M\ KOH\,(aq)$ solution is required to neutralize all of the acid, what was the molarity of the original $H_3PO_4\,(aq)$ solution?

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3. Oxidation States & Oxidation-Reduction Reactions

Question: What is wrong with the following? Note that in (assume acidic) aqueous solution, we an always add H^+(aq) or H_2O(l) to one side of the equation or the other to balance the numbers of H and O atoms.

$$VO^{2+}(aq) \; + \; 2\,MnO_4^-(aq) \quad \longrightarrow \quad VO_2{}^+(aq) \; + \; 2\,Mn^{2+}(aq)$$

In order to make sense of the numbers of atoms of different types which are found to bind themselves together in molecules, it has been convenient to introduce the concept of an "*oxidation state*" for each atom in every molecular or ion. In many (but not all!) cases these *oxidation states* are related to the electronic structure of the atom – the number of electrons it must gain or lose to yield a "closed shell" (see Chapt. 10). A formal definition is that the oxidation state is the charge the atoms would have if all the bonding electrons were transferred to the more "electronegative" element (see Chapt. 10).

Keeping track of this apparent transfer of electrons on forming molecules turns out to be essential for achieving proper balancing of chemical equations in which the oxidation state of some component atoms (or groups) change.

Chemists have developed a set of ordered working rules which allow us to assign an *oxidation state* to each element in a compound.

1. Any pure element has an oxidation state of **zero**.

2. The sum of the oxidation states of all atoms forming a molecule or ion is the **net charge** of that species.

3. In their compounds, group-1 metals have an oxidation state of **+1**

   In their compounds, group-2 metals have an oxidation state of **+2**

4. In its compounds, fluorine always has an oxidation state of **-1**

5. In their compounds, hydrogen atoms have an oxidation state of **+1**, except when combined with group 1 or group 2 metals.

6. In its compounds, oxygen atoms normally have an oxidation state of **-2**, except when O is bonded to O (peroxides):

7. In binary compounds with metals,
   - group 17 elements have oxidation state **-1**
   - group 16 elements have oxidation state **-2**
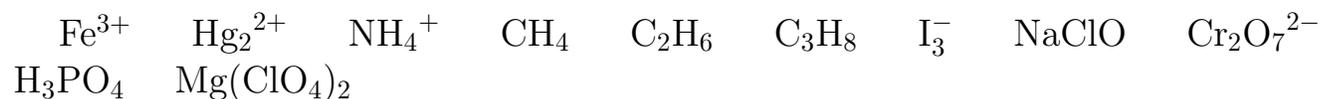   - group 15 elements have oxidation state **-3**

Note:

- When two or more of the above rules are in conflict, the one higher in the list 'wins'.
- Sometimes none of the above rules readily applies. For such cases we can often still use the formal definition. e.g., consider $H-C\equiv N$

- Common polyatomic ions have a characteristic charge (overall oxidation state, or oxidation state sum) which is the same in all of their compounds.
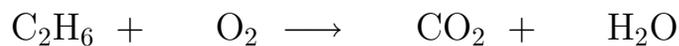
  e.g., SO_4^{2-} $\quad$ NO_3^- $\quad$ NH_4^+ $\quad$ PO_4^{3-} $\quad$ CO_3^{2-}

Exercise 7. Assign oxidation states to each of the elements in the following species.

$\qquad$ Fe^{3+} $\qquad$ Hg_2^{2+} $\qquad$ NH_4^+ $\qquad$ CH_4 $\qquad$ C_2H_6 $\qquad$ C_3H_8 $\qquad$ I_3^- $\qquad$ $NaClO$ $\qquad$ $Cr_2O_7^{2-}$

H_3PO_4 $\qquad$ $Mg(ClO_4)_2$

Oxidation-Reduction ("Redox") Reactions

Redox reactions are reactions in which the oxidation states of two (or more) of the elements change. *e.g.,* (i) combustion reactions

$$C_2H_6 \ + \ \quad O_2 \ \longrightarrow \ \quad CO_2 \ + \ \quad H_2O$$

**(ii) solution reactions sare more complicated !**

In order to obtain a fully balanced result, must keep track of amount of "*oxidation*" and "*reduction*" occurring, since:

- if the oxidation state of an atom *in*creases (i.e., the atom is **oxidized**), the displaced electrons must go somewhere !
- if the oxidation state of an atom *de*creases (i.e., the atom is **reduced**), the electrons must come from somewhere !
- To balance a redox reaction, we must ensure that the electrons lost and gained balance out !

Oxidation/Reduction Half-Reactions

To ensure that the total amount of oxidation equals the amount of reduction (i.e., that the overall number of electrons lost by one type of atom equals the number gained by another), we have to identify and write down the separate **half-reactions** — separate reactions for oxidation and reduction processes which explicitly show the numbers of electrons lost or gained, but *need not be balanced fully w.r.t. species.*

e.g., consider our unbalanced VO^{2+} + MnO_4^- reaction:

$$VO^{2+}(aq) \quad + \quad MnO_4^-(aq) \quad \longrightarrow \quad VO_2^+(aq) \quad + \quad Mn^{2+}(aq)$$
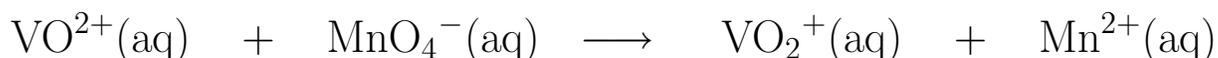
oxidation half-reaction:

reduction half-reaction:

These half-reactions must combine in a way which allows the electrons liberated/gained to cancel out !
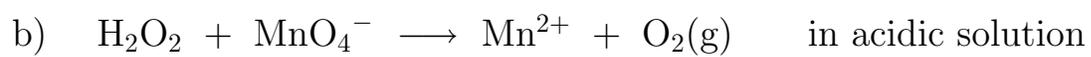
But in any reaction, net charge must balance too !

In any acidic solution have some $H^+(aq)$;   in any basic solution have some $OH^-(aq)$; in a non-acidic/non-basic (acidically neutral) solution we have tiny amounts of both. Thus, we can always balance net charge by adding $H^+(aq)$ to one side of the equation or $OH^-(aq)$ to the other.

Finally ... balance H and O atoms by adding H_2O molecules to one side of the equation or the other.

Summary of Rules for Balancing Redox Equations

1. Assign oxidation states to each element in the reaction, and _identify_ the species being oxidized and reduced.
2. Write separate half reactions for the oxidation and reduction processes.
3. Balance the separate half reactions:

    a) first, with respect to the element being oxidized or reduced, and then

    b) by adding electrons to one side or the other to account for the number of electrons produced (oxidation) or consumed (reduction).
4. Combine the half reactions algebraically so that number of electrons to cancel out. This makes: (**total amount oxidation**) = (**total amount reduction**)
5. If necessary, add $'spectator'$ ions or groups to balance the equation with respect to atoms _other_ than O and H.
6. Balance the net charge by either adding OH^- to one side of the equation (for basic solutions) or H^+ to the other (for acidic solutions).
7. Balance the O and H atoms by adding H_2O .
8. Check the charge balance and the overall mass balance in the final result.

Exercise 8. Complete and balance the equations:

a) $Fe(OH)_3(s) + OCl^- \longrightarrow FeO_4{}^{2-} + Cl^-$ in basic solution

b) $H_2O_2 + MnO_4{}^- \longrightarrow Mn^{2+} + O_2(g)$ in acidic solution

Disproportionation reactions are reactions in which the same species is both oxidized and reduced. *e.g.,*

$$S_2O_3{}^{2-} \quad \longrightarrow \quad S(s) \; + \; SO_2(g)$$

Oxidizing Agents and Reducing Agents

Oxidation and reduction processes must always occur in pairs: if one species is being oxidized, some other species must simultaneously be being reduced (*the electrons must go somewhere!*), and *vise versa*. Some common terms associated with redox reactions illustrate this complementarity.

An **oxidizing agent** (or **oxidant**) is a chemical species which causes some other chemical species to undergo oxidation.

A **reducing agent** (or **reductant**) is a chemical species which causes some other chemical species to undergo reduction.

Strength of an oxidizing agent measures its ability to cause other species to be oxidized.
Strength of a reducing agent measures its ability to cause other species to be reduced.

Many elements have different oxidation states in different compounds: e.g., nitrogen.

species	N atom oxidation state
$NO_3{}^-$	
N_2O_4	
$NO_2{}^-$	
NO	
N_2O	
N_2	
NH_2OH	
N_2H_4	
NH_3	

and the "strength" of these compounds as oxidizing/reducing agents will vary with the oxidation state of the N atom in that species.

Exercise 9. Complete and balance the equations

a) $Cr_2O_7{}^{2-} (aq) + CH_3OH (aq) \longrightarrow Cr^{3+} (aq) + CH_2O (aq)$
   in basic solution

b) $NH_4Cl (aq) + K_2Cr_2O_7 (aq) \longrightarrow CrCl_3 (aq) + N_2 (g)$
   in a weak HCl (acid) solution

c) $P_4 (s) + NO_3^- (aq) \longrightarrow H_2PO_4^- (aq) + NO_2 (g)$
   in an acidic solution

d) $Fe_2S_3 (aq) + O_2 (g) \longrightarrow S (s) + Fe(OH)_3 (s)$
   in a basic solution

Compound or ion	Oxidation state
NO_3^-	+5
N_2O_4	+4
NO_2^-	+3
NO	+2
N_2O	+1
N_2	0
NH_2OH	−1
N_2H_4	−2
NH_3	−3

This species cannot be oxidized further

This species cannot be reduced further

Oxidation half-reaction (reducing agent)

Reduction half-reaction (oxidizing agent)