

SECTION 12

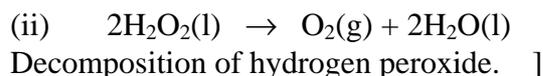
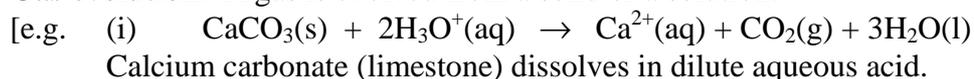
CLASSIFICATIONS OF CHEMICAL REACTIONS

As the number of known chemical reactions is enormous it is useful to be able to describe a particular reaction as belonging to a certain class or classes. Just as a particular individual person could be classified by gender, age, weight, height, colour of eyes, annual income etc., and could fall into several classes, so it is with chemical reaction classification. This section gives the basis of a number of classes. One very important class, that of redox reactions, has an extensive language of its own, and this is introduced. The important classification based on how a reaction occurs is left to *section 16*.

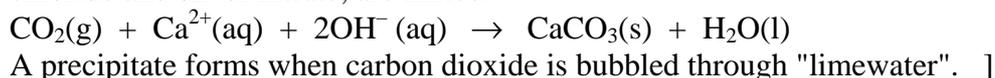
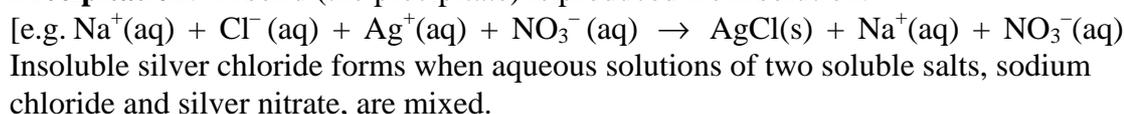
Classification of reactions (the type of reaction) is based on a variety of observations or concepts.

A. Classification based on observation of a phase change

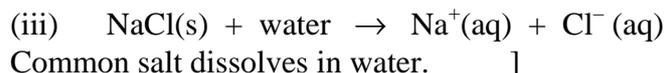
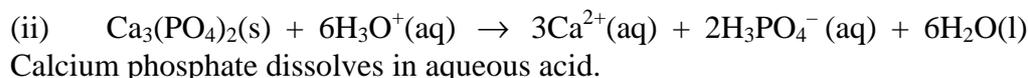
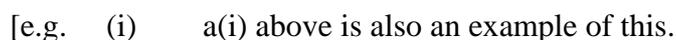
(a) **Gas evolution:** A gas is evolved from a solid or a solution.



(b) **Precipitation:** A solid (the precipitate) is produced from solution.

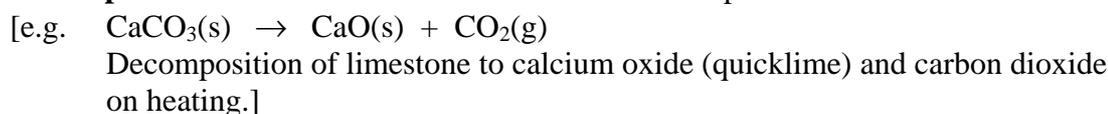


(c) **Dissolution:** A solid dissolves on addition of a reactant or a solvent.



B. Classification based on change in structure of a reactant

(a) **Decomposition:** A substance breaks down to smaller species.

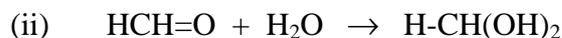


Many reactions may be thought to be between a **substrate** and a **reagent**. The classification is based on the change in structure of the substrate.

- (b) **Addition:** The reagent adds to the substrate, often across a double or triple bond.
[e.g.



Bromine adds across the double bond of ethene (ethylene).



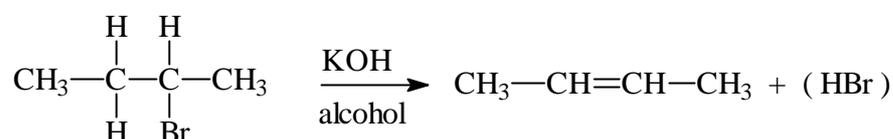
Water adds across the carbonyl double bond of methanal (formaldehyde).



Molecules add to each other to give a molecule of large molar mass called a **polymer**. The process is called **polymerisation**.]

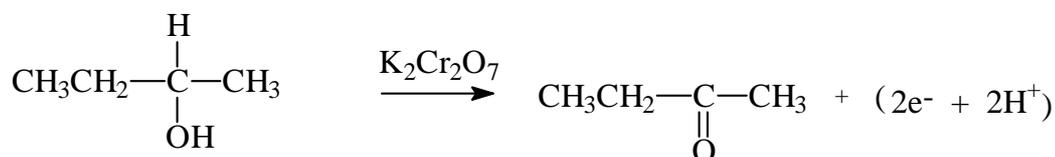
- (c) **Elimination:** Atoms or groups are lost from neighbouring atoms of the substrate with the formation of a double or triple bond. Effectively a small molecule is eliminated.

[e.g. (i)



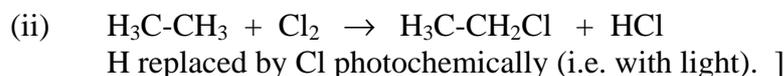
H and Br are eliminated from adjacent carbon atoms.

(ii)



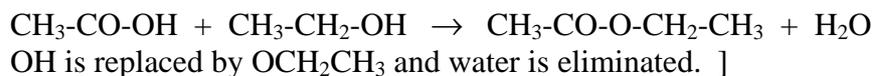
Hydrogen is eliminated from adjacent carbon and oxygen atoms. This loss of two H atoms is more commonly called oxidation. See D, **redox reactions**.]

- (d) **Substitution:** One group on the substrate is replaced by (substituted for) another.
[e.g.



- (e) **Condensation:** Two molecules are joined and a small molecule is eliminated. Condensation can be thought of as particular type of substitution.

[e.g.



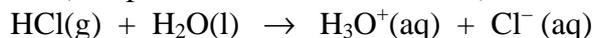
C. Acid-base

Certain hydrogen-containing molecules or ions react by transferring a hydrogen ion, H⁺, to another molecule or ion. The reactant which is the source of the H⁺ is called an **acid**, the reactant to which the H⁺ becomes attached is called a **base**, and the reaction is called **acid-**

base.



The acid hydrogen chloride transfers H^+ to the base ammonia to give the ionic solid ammonium chloride (composed of NH_4^+ and Cl^- ions).



The gas hydrogen chloride acts as an acid as it transfers H^+ to a water molecule which is acting as a base.]

A hydrogen ion, H^+ , is just a proton, and these acid-base reactions are called proton transfer reactions. An **acid** is defined as a **proton donor** and a **base** is defined as a **proton acceptor**. This is the **Brønsted-Lowry** definition. A base must have a non-bonding pair of electrons which can be used to form a bond with a proton.

Brønsted acid: a proton donor, i.e. a species which donates a proton in a chemical reaction [e.g. HCl in the above examples].

Brønsted base: a proton acceptor, i.e. a species which accepts a proton in a chemical reaction [e.g. NH_3 and H_2O in the above two examples].

Oxonium (hydronium) ion: the cation H_3O^+ , often written as $\text{H}^+\text{(aq)}$ or just H^+ in equations in water (water, aqua, aq). It is important to realise the **proton**, H^+ , does not exist as such in condensed matter, i.e. liquid or solid state. The term hydronium is still widely used

Hydroxide ion: the anion OH^- . (As it is the O which has the formal charge of -1, HO^- would be a more correct formula, but OH^- is usually written).

Conjugate acids and bases: When an acid loses a proton, its product is called the conjugate base of that acid. When a base accepts a proton its conjugate acid is formed [e.g. HCl/Cl^- , $\text{NH}_4^+/\text{NH}_3$, $\text{H}_3\text{O}^+/\text{H}_2\text{O}$, and $\text{H}_2\text{O}/\text{OH}^-$ are conjugate acid-base pairs].

Neutralisation: The reaction between an acid and a base [e.g. reaction of aqueous HCl and NaOH to give NaCl and H_2O].

Salt: the product (other than water) of a neutralisation reaction between an acid and a base. Salts are ionic compounds [e.g. NaCl in the above neutralisation reaction].

Alkali: Aqueous solution of a base [e.g. aqueous NaOH or aqueous ammonia].

D *Oxidation-reduction (redox) reactions*

Redox reaction: A reaction in which one reactant is **oxidised** and another is **reduced**. The concept of oxidation and reduction plays a very important role in chemistry. Historically a compound was said to be oxidised if it gained oxygen and reduced if it lost oxygen. The term **oxidation** was later extended to include the loss of hydrogen, and **reduction** to include the gain of hydrogen. However with the development of the electronic structure of the elements the definitions were changed in order to encompass a wider range of reactions than just those involving loss or gain of oxygen or hydrogen:

Oxidation: a process in which a species loses electrons [e.g. $\text{Cu} \rightarrow \text{Cu}^{2+}$].

Reduction: a process in which a species gains electrons [e.g. $\text{Cu}^{2+} \rightarrow \text{Cu}$].

In a **redox reaction** one reactant called the **oxidant** (older term **oxidising agent**) oxidises a second reactant called the **reductant** (older term **reducing agent**) and is itself reduced.

[e.g. $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ Zinc is the reductant and copper ions the oxidant
 $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$ Chlorine is the oxidant and bromide ions the reductant.]

Half-reactions: Redox reactions may be separated into two half-reactions, one involving oxidation (loss of electrons) and the other reduction (gain of electrons).

[e.g. for the above two examples:

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	oxidation
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	reduction
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	reduction
$2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$	oxidation]

In a balanced half-reaction equation the number of atoms of each element and the total charge must be the same on each side of the equation.

Balanced redox equation: One in which there are no free electrons on either side of the reaction equation. If two half-equations (one oxidation and one reduction) with different numbers of free electrons are added to give an overall redox equation, the equations must be multiplied by integers so that the electrons cancel on addition.

[e.g. For the reaction $\text{Zn} + \text{Ag}^+ \rightarrow \text{Zn}^{2+} + \text{Ag}$

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	oxidation	
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	reduction	x 2 and add
$\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$]		

Oxidation number (oxidation state): A concept central to redox chemistry.

Electronegativity: A measure of the power of an atom to attract electrons to itself when it is part of a compound. The order of electronegativity of common elements is:



Rules for oxidation number (state): The oxidation number of an atom in a substance may be determined from the following rules:

1. The oxidation number of an atom in an element is zero.
2. The oxidation number of an atom in a monoatomic ion equals the charge on the ion.
3. Oxygen has the oxidation number of -2, except in peroxides (-1) and when bound to fluorine (+2).
4. Hydrogen has an oxidation number of +1 except in metal hydrides(-1).
5. Halogens have oxidation number -1 except in oxygen-halogen species.
6. The sum of the oxidation numbers of the atoms in a polyatomic species equals the charge on that species.

When an atom in a species has an oxidation number x it is said to be in the x oxidation state. The above rules, which usually give the correct number, are based on the general concept "*the oxidation number of the atom in a species is the charge it would have in the most probable ionic formulation of that species*". Putting this another way, it is assumed that all the electrons of a particular bond reside on the atom with the greater electronegativity. So an overall rule to determine oxidation numbers is: write the Lewis structure of the species and count the number of valence electrons on each atom assuming the bonding electrons reside on the more electronegative atom, and compare the number with that of the neutral atom; the difference is the oxidation number. [e.g. HCl ; H-Cl ; $\text{Cl} > \text{H}$; H has 0 electrons; Cl has 8

valence electrons: H, +1; Cl, -1 SiH₄; H-SiH₃; H>Si, each H has 2 valence electrons, Si has 0 valence electrons: H, -1; Si, +4].

The concept of oxidation state plays a major role in the classification of inorganic compounds, but understanding of its significance and usefulness comes only with experience.

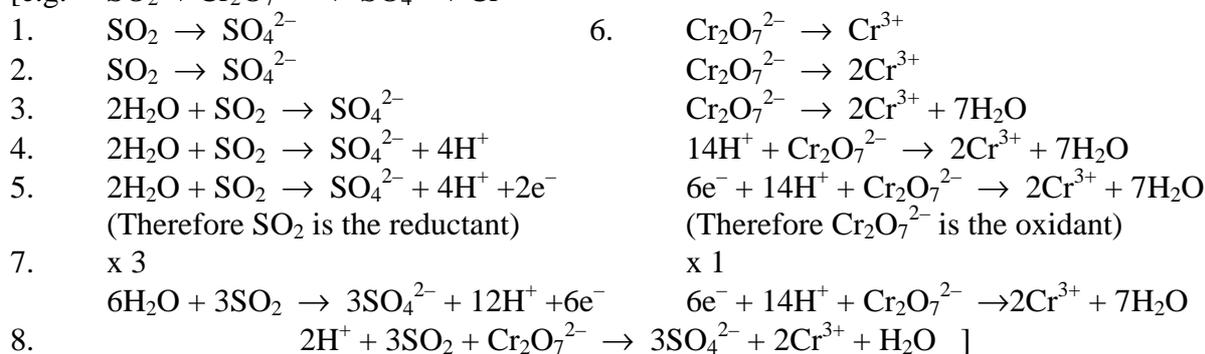
A Roman numeral is often used in the name of a species to indicate the oxidation state. [e.g. The compounds CrCl₃ and Na₂CrO₄ are called chromium(III) chloride and sodium tetraoxochromate(VI) respectively. See *section 13*.]

In redox reactions the oxidation number of an atom in the oxidant decreases, while that of an atom in the reductant increases. [e.g. In the examples above the oxidation state of zinc has increased from 0 to +2, that of bromine has increased from -1 to 0, that of chlorine has decreased from 0 to -1, and that of silver has decreased from +1 to 0.]

Rules for balancing redox equations: The ability to write balanced redox equations is an essential skill. This can be done by following a simple set of "book-keeping" rules:

1. Write down the formula for one of the reactants on the left and the formula for its product on the right of an arrow.
2. Balance all elements other than oxygen and hydrogen.
3. Balance oxygens by adding H₂O to the appropriate side.
4. Balance hydrogens by adding H⁺ to the appropriate side.
5. Balance charge by adding electrons to the appropriate side.
This gives a balanced half-equation. If the electrons are on the right-hand side, the reactant is the reductant (lost electrons and therefore has been oxidised). If the electrons are on the left-hand side the reactant is the oxidant (has gained electrons and therefore has been reduced).
6. Repeat rules 1-5 for the other reactant.
7. Multiply the two half equations by integers so that the number of electrons shown in each half-equation is the same.
8. Add the two half-equations, cancelling equal number of species that occur on both sides. The result is the balanced redox equation.

[e.g. SO₂ + Cr₂O₇²⁻ → SO₄²⁻ + Cr³⁺

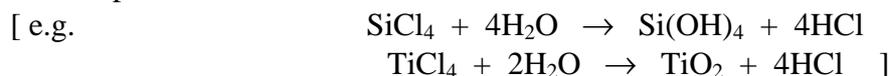


A useful check when balancing redox equations is to note that the number of electrons in each half-reaction is the same as the changes in oxidation numbers.

E. *Hydrolysis*

Reaction between a compound and water which results in the making or breaking of the O-H bonds of water [e.g. the reaction of hydrogen chloride and water to give hydrochloric acid,

section 12-3]. However, the term is more commonly used for reactions resulting in the breaking of O-H bonds of water and the formation of a bond between the O of the water and the compound.



F. *Classification based on the mechanism of a reaction*

This topic is covered in *section 16*.

EXERCISES

The following reactions can all be classified in more than one of the classes given in this section. Give two classifications for each. The equations are not all balanced.

- $$\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3$$
- $$2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$$
- $$\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$$
- $$(\text{CH}_3)_2\text{CHCH}_2\text{Br} + \text{OH}^- \rightarrow (\text{CH}_3)_2\text{C}=\text{CH}_2 + \text{Br}^- + \text{H}_2\text{O}$$
- $$\text{MnO}_4^- (\text{aq}) + \text{Mn}^{2+}(\text{aq}) \rightarrow \text{MnO}_2(\text{s})$$
- $$\text{Cu}^{2+}(\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{CuI}(\text{s}) + \text{I}_2(\text{s})$$

Give the oxidation number (state) of the italicised atom in each of the following species.

7. NH_3 8. CaCl_2 9. SO_3 10. H_2O_2 11. ClO_3^- 12. $\text{Cr}_2\text{O}_7^{2-}$

Balance the following redox reactions in aqueous solution. (aq has been omitted from the formulae for the dissolved ions.)

- $$\text{Cl}_2 + \text{Fe}^{2+} \rightarrow \text{Cl}^- + \text{Fe}^{3+}$$
- $$\text{MnO}_4^- + \text{Br}^- \rightarrow \text{Mn}^{2+} + \text{Br}_2$$
- The reaction of question 5 above
- $$\text{Zn} + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{ZnSO}_4 + \text{FeSO}_4$$

(Identify the **spectator ions** (i.e. those ions which are not taking part in the redox reaction), balance the essential ionic reaction and add the spectator ions at the end. Balanced equations in this form are needed in analytical determinations.)