Chem Factsheet

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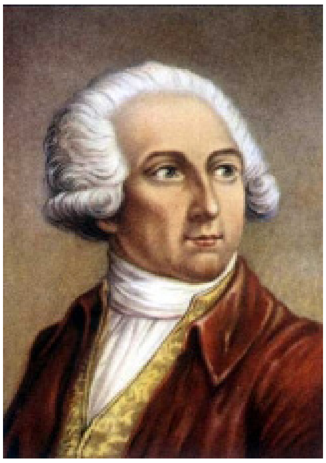
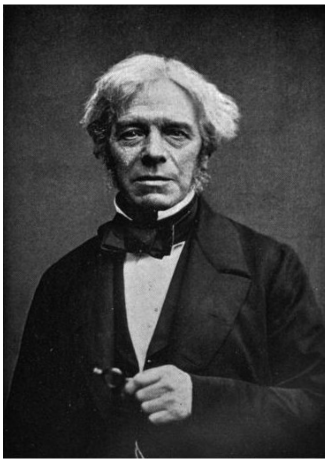
How To Calculate Oxidation Numbers

From the very early days of chemistry, scientists such as Joseph Priestley and Antoine Lavoisier (1743-1794) were very interested in the behaviour of the element, oxygen. This was probably because it was readily available in the air and the process of burning was "easy" to investigate. Hence, Lavoisier was probably responsible for first introducing of the term "**oxidation**" as meaning, quite literally, a **chemical combination with oxygen** to produce one or more oxides.


Joseph Priestley
(1733-1804)


Antoine Lavoisier
(1743-1794)


Michael Faraday
(1791-1867)

e.g. Magnesium is **oxidised** to magnesium oxide when it burns in oxygen
$2Mg(s) + O_2(g) \rightarrow 2MgO$

e.g. Methane is **oxidised** to carbon dioxide and water when it burns in oxygen
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

This also led to the term meaning the opposite of oxidation, **"reduction"– the removal of oxygen from a substance**.

e.g. Copper(II) oxide is **reduced** by carbon to form copper and carbon dioxide or carbon monoxide
$2CuO + C$ (or **2C**) $\rightarrow 2Cu + CO_2$ (or **2CO**)

Looking at the affinity of oxygen for hydrogen to form water
$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$, since the hydrogen is being oxidised (oxygen added), it seemed reasonable to say the oxygen is reduced. This led to an alternative definition of **reduction – the chemical addition of hydrogen** to a substance – and hence another definition for **oxidation – the removal of hydrogen**.

e.g. Ethene is **reduced** to ethane by reaction with hydrogen
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

e.g. Hydrogen chloride is **oxidised** to chlorine by removal of hydrogen
$2HCl(g) \rightarrow Cl_2(g) + H_2(g)$

As bonding theories developed, particularly ionic bonding, it became apparent that reactions such as:
$2CuO + C \rightarrow 2Cu + CO_2$
and $CuCl_2(l) \rightarrow Cu(s) + Cl_2(g)$ by electrolysis
and $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$
are all similar in that a copper compound is being changed to copper in all cases. Hence, since the first of these is a reduction (removal of O) the others should also be reductions.
The ionic nature of the copper compounds suggested that the "common factor" amongst these reactions is actually the conversion of copper ions (Cu^{2+}) to copper atoms by addition of 2 electrons.

i.e. $Cu^{2+} + 2e^- \rightarrow Cu$
Hence, yet another definition was formulated – **reduction is the addition of electrons**. In line with this, oxidation was also redefined - **oxidation is the removal (loss) of electrons**.

Summary

	Oxidation	Reduction
1	Gain of oxygen	Loss of oxygen
2	Loss of hydrogen	Gain of hydrogen
3	Loss of electrons	Gain of electrons

This multiplicity of definitions for the same concepts was soon seen to be unacceptable. Whilst definitions 1 and 3 can be applied to:
$2Mg(s) + O_2(g) \rightarrow 2MgO$ because $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$ is involved, definition 2 is not applicable.

Equally, definitions 1 and 2 can be applied to:
$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

but definition 3 seems inappropriate for these covalent substances. What was needed was one definition for all cases!

Oxidation Numbers or Oxidation States

Michael Faraday (see earlier) was responsible for formulating the "**oxidation number / state system**" to give a **single definition** to allow **any** oxidation or reduction reaction to be recognised and classified.

The basic idea was to use a **set of rules** to **assign a number** (the atom's oxidation state / number) to **each and every atom** in a substance. This oxidation state / number is the ***hypothetical*** charge that the atom would have if all its bonds to other atoms were 100% ionic. Hence, the same rules apply both to ionic and covalent substances.

Oxidation states are typically represented by whole numbers (integers), which can be positive, negative, or zero. However, in some cases, an **average oxidation state** of the element results from applying the rules and is a fraction (see later).
The highest known oxidation state is +8 while the lowest known oxidation state is −4.

Rules for deriving oxidation states

Rule 1: In all **UNCOMBINED ELEMENTS**, an atom's oxidation state equals zero (0)

Rule 2. In all **COMPOUNDS**, the **sum** of all the oxidation states of all the atoms equals zero.

Rule 3. In all **IONS**, the **sum** of all the oxidation states of all the atoms equals the charge on the ion.

Rule 4. In all **COMPOUNDS**, group 1 elements have oxidation state +1, group 2 elements have oxidation state +2, group 3 elements have oxidation state +3 and fluorine (F) has oxidation state -1.

Rule 5. In **most COMPOUNDS hydrogen** has an oxidation state of **+1** except in metal hydrides (MH_n) where the metal M will have the positive oxidation state (+n) and H will be -1.

Rule 6. In **most COMPOUNDS oxygen** has an oxidation state of **-2** except in fluorine oxide (F_2O) where F must be -1 (rule 4) causing O to be +2 and peroxides (O_2^{2-}) where the oxidation state is -1 (rule 3).

Rule 7. **HALOGENS** other than fluorine have an oxidation state of −1 except when they are bonded to oxygen, nitrogen, or another more electronegative halogen.

Rule 8. In **BINARY COMPOUNDS** (contain 2 elements only) the more electronegative element is assigned the negative oxidation state.

Remember there is a hierarchy in these rules, descending in priority from 1 to 8.. Hence, because earlier rules must be given priority, the "exceptions" occur in rules 5 - 7.

Remember to attach "+" or "-" to the oxidation states, especially the positive ones.

Avoid the use of "n+ or n-" instead of "+n and –n" ; the former represent charges while the latter are numbers and represent oxidation states.

By Rule 3, for monatomic ions, the ionic charge and the oxidation state will be numerically equivalent but not identical!

Ion	Charge	Oxidation State (OS)
Iron(III) ; Fe^{3+}	3+	+3
Sulphide ; S^{2-}	2-	-2

Usually, the rules will allow all but one of the different atoms in a compound or compound ion to be assigned an oxidation state. The other is the calculated using rule 2 or 3.

Examples

OS(X) refers to the oxidation state of atom X.

Particle	Name	Rule(s)	Working	Answer(s)
Cl_2	Chlorine	1	None	Cl(0)
Ca^{2+}	Calcium ion	3	None	Ca(+2)
Al^{3+}	Aluminium ion	3	None	Al(+3)
Br^-	Bromide ion	3	None	Br(-1)
N^{3-}	Nitride ion	3	None	N(-3)
HCl	Hydrogen chloride	5 then 2	(+1) + OS(Cl) = 0	H(+1) ; Cl(-1)
NaBr	Sodium bromide	4 then 2	(+1) + OS(Br) = 0	Na(+1) ; Br(-1)
CO_2	Carbon dioxide	6 then 2	OS(C) + 2(-2) = 0	O(-2) ; C(+4)
NH_3	Ammonia	5 then 2	OS(N) + 3(+1) = 0	H(+1) ; N(-3)
BrCl	Bromine chloride	7&8 then 2	OS(Br) + (-1) = 0	Cl(-1) ; Br(+1)
NH_4^+	Ammonium ion	5 then 3	OS(N) + 4(+1) = +1	H(+1) ; N(-3)
NO_3^-	Nitrate ion	6 then 3	OS(N) + 3(-2) = -1	O(-2) ; N(+5)
CO_3^{2-}	Carbonate ion	6 then 3	OS(C) + 3(-2) = -2	O(-2) ; C(+4)
$S_2O_3^{2-}$	Thiosulphate ion	6 then 3	2OS(S) + 3(-2) = -2	O(-2) ; S(+2)
C_3H_8	Propane	5 then 2	3OS(C) + 8(+1)) = 0	H(+1) ; C(-8/3)
CH_3OH	Methanol	5&6 then 2	OS(C) + 4(+1) + (-2) = 0	H(+1) ; O(-2) ; C(-2)
HCOOK	Potassium methanoate	5&6 then 2	(+1) + OS(C) +2(-2) + (+1) = 0	H(+1) ; O(-2) ; K(+1) ; C(+2)
MnO_4^-	Manganate(VII) ion	6 then 3	OS(Mn) + 4(-2) = -1	O(-2) ; Mn(+7)
H_2SO_4	Sulphuric acid	5&6 then 2	2(+1) + OS(S) + 4(-2) = 0	H(+1) ; O(-2) ; S(+6)
ICl_3	Iodine trichloride	7&8 then 2	OS(I) + 3(-1) = 0	Cl(-1) ; I(+3)

Practice Questions

1. Work out the oxidation states of each of the atoms in each of the following compounds.

1 BrF_5	2 Mn_2O_3	3 $Na_2C_2O_4$	4 $K_2Cr_2O_7$	5 XeO_4
6 $S_2O_8^{2-}$	7 CH_3CH_2CHO	8 PCl_4^+	9 CrO_4^{2-}	10 $Na_2S_4O_6$

New definitions

Having worked out the oxidation states involved (see above), if:

A a particle (atom, ion or molecule) contains an atom which undergoes an **INCREASE in oxidation state**, then that particle is said to have been **OXIDISED**.

B a particle (atom, ion or molecule) contains an atom which undergoes an **DECREASE in oxidation state**, then that particle is said to have been **REDUCED**.

C a particle (atom, ion or molecule) contains an atom which undergoes an **BOTH A DECREASE AND AN INCREASE in oxidation state**, then that particle is said to have been **DISPROPORTIONATED**.

2. Work out the oxidation states of each of the atoms in each of the following pairs of compounds and hence decide whether the first substance is oxidised, reduced or neither to form the second substance.

1	$CuCl_2 \rightarrow CuCl$	2	$C_4H_{10} \rightarrow CO_2$
3	$ClO_4^- \rightarrow Cl^-$	4	$NH_3 \rightarrow NH_4^+$
5	$Br_2 \rightarrow BrO_3^-$	6	$CH_3OH \rightarrow HCOOH$
7	$K_2CrO_4 \rightarrow K_2Cr_2O_7$	8	$MnO_4^- \rightarrow Mn^{2+}$
9	$Al(OH)_6^{3-} \rightarrow Al(H_2O)_6^{3+}$	10	$VO^{2+} \rightarrow VO_3^-$

3. Quoting relevant oxidation states, explain why the following reaction is a disproportionation reaction.

$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$

Answers

1.

1	F(-1) ; Br(+5)	2	O(-2) ; Mn(+3)
3	Na(+1) ; O(-2) ; C(+3)	4	K(+1) ; O(-2) ; Cr(+6)
5	O(-2) ; Xe(+8)	6	O(-2) ; S(+7)
7	H(+1) ; O(-2) ; C(-4/3)	8	Cl(-1) ; P(+5)
9	O(-2) ; Cr(+6)	10	Na(+1) ; O(-2) ; S(+5/2)

2.

1	Cu(+2) → Cu(+1) ; Reduced	2	C(-5/2) → C(+4) ; Oxidised
3	Cl(+7) → Cl(-1) ; Reduced	4	N(-3) → N(-3) ; Neither
5	Br(0) → Br(+5) ; Oxidised	6	C(-2) → C(+2) ; Oxidised
7	Cr(+6) → Cr(+6) ; Neither	8	Mn(+7) → Mn(+2) ; Reduced
9	Al(+3) → Al(+3) ; Neither	10	V(+4) → V(+5) ; Oxidised

3. The oxidation state of chlorine changes simultaneously from 0 in Cl_2 to (-1) in NaCl and (+1) in NaClO.
The conversion to NaCl is therefore a reduction while the conversion to NaClO is an oxidation.
Since the same atom (Cl) is both oxidised and reduced in the same reaction, Cl_2 is said to be disproportionated.

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