Oxidation – Reduction and Electrochemistry

Definitions Oxidation and Reduction

Oxidation: Oxidation is the **loss of electrons** by an atom or ion.

Reduction: Reduction is the **gain of electrons** by an atom or ion.

Oxidizing agent (oxidant): This substance, (atom, molecule or ion), causes oxidation. i.e. causes the loss of electrons from the substance being oxidized. (Thus the oxidizing agent gains electrons in the process and is itself reduced.)

Reducing agent (reductant): This substance, (atom, molecule or ion), causes reduction. i.e. causes the gain of electrons to the substance being reduced. (Thus the reducing agent loses electrons in the process and is itself oxidized.)

Oxidation and reduction occur together. In an **oxidation – reduction** reaction or **redox** reaction, electrons pass from the reducing agent to the oxidising agent.

See p.148 in Harwood & Petrucci

Redox reactions consist of two **half reactions** which must occur together, the oxidation half-reaction and the reduction half-reaction. ***See p.142/3 in Harwood & Petrucci for an example.***

e.g. oxidation: $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$

e.g. reduction: $2Ag^+_{(aq)} + 2e^- \longrightarrow 2Ag_{(s)}$

Overall reaction: $Cu_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$

In this reaction, a piece of copper wire will "grow" silver metal crystals from a solution of silver nitrate while the blue copper ions dissolve in solution as they are produced. Copper metal is **oxidized** (and is the **reducing agent**). Silver ions (aq) are **reduced** (and is the **oxidizing agent**).

e.g. oxid: $Mg_{(s)} \longrightarrow Mg^{2+}_{(g)} + 2e^-$ (loss of electrons)

e.g. red: $Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(g)}$ (gain of electrons)

Overall: $Mg_{(s)} + Cl_{2(g)} \longrightarrow Mg^{2+} + 2Cl^-_{(g)}$

$Mg^{2+}_{(g)} + 2Cl^-_{(g)} \longrightarrow MgCl_{2(s)}$ + Energy (exothermic)

Heated magnesium metal will readily combine with chlorine to form the salt magnesium chloride. The reaction is self-sustaining once started. ((Magnesium, a Group II metal tends to lose $2e^-$ to acquire noble gas configuration, while Chlorine, a Group VII non-metal tends to gain $1e^-$ to reach noble gas configuration.)

OIL RIG
Oxidation **I**s **L**oss
Reduction **I**s **G**ain

LEO GER
Lose **E**lectrons – **O**xidation
Gain **E**lectrons – **R**eduction

Reduction and **Ox**idation reactions always occur concurrently – you can't have one without the other, .: they are often called **REDOX** reactions.

Oxidation Numbers

To follow the loss and gain of electrons in complicated reactions, we utilize the concept of **oxidation numbers**. It is similar to valence, a term you learned in Grade 11. A method of expressing the valence or the combining power of elements is the idea of **oxidation number** or **oxidation state**. Each atom is given a signed number (plus, minus or zero) according to the following rules:

Rules for assigning oxidation numbers

1. All elements have an oxidation number of zero. e.g. O_2, Ca, Al, Na, S_8, I_2 all have an O.N of Zero.
2. All monatomic ions have an oxidation number equal to their charge. e.g. Cl^- has an O.N. of –1, Mg^{2+} has an O.N. of +2 etc.
3. The sum of the oxidation numbers in a molecule is zero. e.g. CO_2 has a sum of zero, with C being +4 and O being –2.
4. The sum of the oxidation numbers in a polyatomic ion is the charge of that ion. e.g. in CO_3^{-2}, the carbonate ion, Carbon is +4 and Oxygen is –2.
5. Generally, the oxidation number of oxygen in compounds is –2. (The exceptions are peroxides where it is -1, and in combination with fluorine it is +2)
6. Generally, the oxidation number of hydrogen in compounds is +1. (The exception is the hydride ion, where H is –1)
7. Generally, the ions of the alkali metals (group I) have an oxidation number of +1, while the ions of the alkaline-earth metals (group II) have an oxidation number of +2. {Al3+}

The non-metals can have a variety of oxidation numbers. e.g. Chlorine has the oxidation numbers –1,0,+1,+3,+5,+7

In a chemical reaction, the net change in oxidation numbers must be zero.

Oxidation is an increase in oxidation number while **reduction** is a decrease in oxidation number.

Oxidation

__________________\
/

-5 -4 -3 -2 -1 0 + 1 +2 +3 +4 +5

/____________________
\ Reduction

1. What is the oxidation number of N in the following:

a) N_2 B) NO_2 c) N_2O_4 d) HNO_2 e) HNO_3 f) NO^+ g) N^{-3} h) NO_3^- I) NO_2^- J) NH_3 k) $Cu(NO_3)_2$ (l) $Fe(NO_2)$

2. What is the oxidation number of: a) Cr in $Cr_2O_7^{-2}$ b) Mn in MnO_4^- c) Au in Au_2O_3 d) Ce in $Ce(SO_4)_2$ e) Bi in Bi_2O_5 f) N in NH_4^+ g) Mn in MnF_3 h) U in U_3O_8 (i) P in H_3PO_4 (j) Cl in Ca $(clO_4)_2$ (k) Mn in $KMnO_4$ (l) Fe in $Fe_2(SO_4)_3$ (m) Cr in Cr $(CN)_6^{-3}$ (n) As in As_2O_3, AsO_2^{-1}, AsO_4^{-3}, AsH_3 (o) I in I^{-1}, IO^{-1}, IO_3^{-1}, I_2, ICl_3, ICl_2^{-1}

The Electrochemical Series of Metals

K			Potassium			K	
Ba			Barium			Ba	
Sr			Strontium	soluble		Sr	liberate H_2 from
Ca			Calcium			Ca	cold water
Na	extremely		Sodium		never	Na	
Mg	difficult		Magnesium			Mg	liberate H_2
Al			Aluminum			Al	from steam
Mn			Manganese			Mn	
Zn			Zinc			Zn	liberate H_2
Cr			Chromium			Cr	from acids
Fe		oxides	Iron			Fe	
Cd		stable	Cadmium			Cd	
Co			Cobalt	rarely		Co	
Ni	difficult		Nickel			Ni	
Sn			Tin			Sn	
Pb			Lead	insoluble		Pb	
H			Hydrogen			H	
Cu			Copper			Cu	attacked by
As			Arsenic			As	oxidizing acids
Bi			Bismuth			Bi	
Sb	easy		Antimony	frequently		Sb	do not liberate
Hg			Mercury			Hg	H_2 from acids
Ag		oxides	Silver			Ag	
Pt		decompose	Platinum	usually		Pt	not attacked by
Au			Gold			Au	common acids
reduction of oxides by hydrogen		**effect of heat on oxides**		**solubility of oxides in water**		**found free in nature**	

Problem Assignment

Give products for the following reactions where a reaction occurs. If no reaction occurs, write N.R. (no reaction).

1. $Cu + Na^{+} \longrightarrow$
2. $K + HCl \longrightarrow$
3. $Ca + Cr^{3+} \longrightarrow$
4. $Ag + Cu^{2+} \longrightarrow$
5. $Zn + Al^{3+} \longrightarrow$
6. $K + Ag \longrightarrow$
7. $ZnO + H_2 \longrightarrow$
8. $Mn + HCl \longrightarrow$
9. $H_2 + Ag_2O \longrightarrow$
10. $Ba + Na^{+} \longrightarrow$
11. $Na^{+} + Mn^{2+} \longrightarrow$
12. $Fe^{2+} + Sn \longrightarrow$
13. $Ni + Hg^{2+} \longrightarrow$
14. $Fe_2O_3 + H_2 \longrightarrow$
15. $Sn + Au^{3+} \longrightarrow$
16. $Mg^{2+} + Na \longrightarrow$
17. $Al + Cu_{2+} \longrightarrow$
18. $Fe + Ni \longrightarrow$
19. $Na_2O + H_2 \longrightarrow$
20. $CaO + Heat$
21. $Ag_2O + Heat \longrightarrow$
22. $Cu + HCl \longrightarrow$
23. $Ni + \text{cold } H_2O \longrightarrow$
24. $Al_2O_3 + Heat \longrightarrow$
25. $Al + \text{warm } H_2O \longrightarrow$
26. $CuSO_4 + Zn \longrightarrow$
27. $CaCl_2 + Mg \longrightarrow$
28. $SnCl_2 + Ag \longrightarrow$
29. $Al + CoCl_2 \longrightarrow$
30. $AgNO_3 + Cd \longrightarrow$

31. Place a check in the appropriate box below if:
    a. the metal reacts with cold water;
    b. the metal reacts with steam;
    c. the metal reacts with hydrochloric acid;
    d. the oxide of the metal decomposes when heated;
    e. the oxide of the metal is reduced by hydrogen;
    f. the metal displaces tin from a stannous chloride solution;
    g. the metal displaces copper from a cupric sulfate solution;

	aAaaa	B	C	D	E	F	G	
Mg								
Ag								
Hg								
Na								
Al								
Pb								
Fe								

32. Using the electrochemical series:
    a. Name 2 reducing agents better than Ni.
    b. Name 2 oxidizing agents better I_2.
    c. Name 1 oxide that can be reduced by hydrogen.
    d. Name 1 oxide that cannot be reduced by hydrogen.
    e. Name 2 substances that can be oxidized by the O_2 of the air.
    f. Name 1 oxide that decomposes on heating.
    g. Name 2 oxides that do not decompose on heating.
    h. Name 2 substances that will oxidize I^{-1}.
    i. Name 2 substances that will reduce I_2.
    j. Name 2 substances that will reduce Pb^{+2}.
    k. Name 2 substances that will oxidize Pb.

Oxidizing and Reducing Agents

An oxidizing agent is something that causes oxidation, i.e. an increase in the oxidation state of another substance and is itself reduced . It is therefore a good electron acceptor. The cheapest oxidizing agent is: _____.

Most oxidizing agents are rich in oxygen. They accept electrons readily, therefore losing oxygen as oxide. Chlorine also works well producing chloride.

A reducing agent is something that causes reduction i.e. a decrease in the oxidation state of another substance and is itself oxidized . It must therefore be a good electron donor. The most common reducing agent is hydrogen, H_2. Another good reducing agent is $LiAlH_4$ (releases H^-), useful in organic chemistry.

The activity series introduced earlier is a list of metals in the order of decreasing strength as reducing agents. Elemental metals are reducing agents in most of their reactions. The active metals of the sodium family and also calcium, barium and strontium are very good reducing agents. Other good reducing agents are Mg and Al.

How can an atom, molecule, or ion be recognized as a potential oxidizing agent or reducing agent? An oxidizing agent must contain an atom that can have a lower oxidation number, otherwise no reduction is possible. Similarly, a reducing agent must contain an atom that can have a higher oxidation number.

Here is a list of **oxidizing agents**:

Permanganates	MnO_4^-
dichromates	$Cr_2O_7^{-2}$
chlorates	ClO_3^-
perchlorates	ClO_4^-
bromates	BrO_3^-
iodates	IO_3^-
hypochlorites	ClO^-
Halogens	F, Cl, Br, I
nitrates	NO_3^-
Hydrogen peroxide	H_2O_2
Oxygen / Ozone	O_2, O_3
Metal dioxides (Pb, Mn)	

Reducing Agents

H_2 metal hydrides metals carbon sulphites iron (II) salts

SO_2 $SnCl_2$ H_2S NO_2^- CO