

Oxidation and Reduction

C020

A broad class of reactions in chemistry involves the exchange of electrons and are known as **reduction-oxidation** (redox) reactions

An atom is **oxidized** when it **loses** electrons, and **reduced** when it **gains** electrons

An oxidation process is always accompanied by a reduction process

Divide these reactions into two halves that represent the corresponding loss and gain of electrons

Examples of **oxidation** half reactions:



Examples of **reduction** half reactions:



Two mnemonics to remember this:

OIL RIG = oxidation is loss; reduction is gain

LEO GER = lose electrons oxidize; gain electrons reduce

The species supplying the electron is said to be the reducing agent
(which itself is oxidized)

The species accepting electrons is said to be the oxidizing agent
(which is itself reduced)

Redox Reactions

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Oxidation numbers

An oxidation number (ON) represents "the number of electrons theoretically lost or gain by each atom in a molecule during a reaction"

ON can (and usually are) integers but they also can be fractional!

How to assign oxidation numbers

1.) All neutral elements and their allotropes have an ON = 0

For example: O_2^0 , O_3^0 , Cl_2^0 , Fe^0 , S_8^0

2.) For monatomic ions, ON = ion charge

For example: $O^{2- (-2)}$, $Al^{3+ (+3)}$, $Na^{+ (+1)}$

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3.) In a polyatomic species, individual ONs are usually as follows in order of importance:

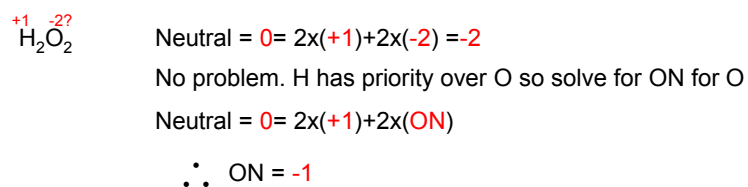
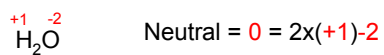
- i) F = -1
- ii) Group I metals = +1 (Li, Na, K, Rb, Cs)
- iii) Group II metals = +2 (Be, Mg, Ca, Sr, Ba)
- iv) H = +1
- v) O = -2
- vi) Group VII halogens = -1 (Cl, Br, I)

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4.) In a polyatomic species the sum of all individual ONs = overall charge on the species

Examples:



The O in peroxide forms an exception to the expectations of point 3).

Redox Reactions

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$$\text{Net charge} = -1 = 2 \times (+1) + \text{ON(P)} + 4 \times (-2)$$

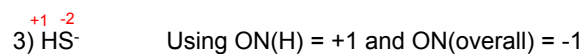
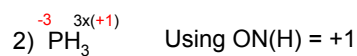
$$\therefore \text{ON(P)} = -1 - 2 + 8 = +5$$

In general groups I and II and other metals act as reducing agents; that is, they donate electrons, and groups VI and VII act as oxidizing agents; that is, they accept electrons

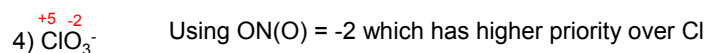
Redox Reactions

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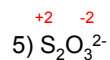
More examples



$$(+1) + \text{ON(S)} = -1 \quad \therefore \text{ON(S)} = -2$$



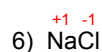
$$\text{ON(Cl)} + 3 \times (-2) = -1 \quad \therefore \text{ON(Cl)} = +5$$



Using ON(O) = -2

$$2 \times \text{ON(S)} + 3 \times (-2) = -2 \quad \therefore 2 \times \text{ON(S)} = +4$$

$$\text{ON(S)} = +2$$



Using ON(group I) = +1 and/or ON(group VII) = -1

Redox Reactions

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Balancing Redox Equations

There are a number of ways to balance redox reactions; we will use the half-reaction method since it does not require judging which species is reduced or oxidized

A redox equation is fully balanced only when

- 1.) there is a complete mass balance
- 2.) the # electrons liberated by the reducing agent = the # electrons accepted by the oxidizing agent

Half-Reaction Method Steps

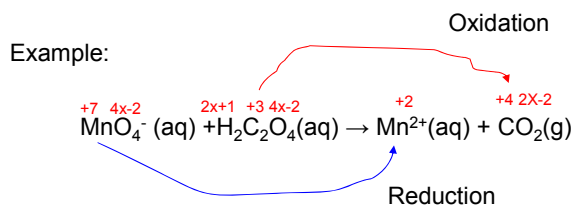
1.) Recognize the reaction as an oxidation-reduction process and separate the reaction, preferably written in ionic form, into two half reactions: one an **oxidation**, the other a **reduction**

This can usually be done by inspection, but oxidation numbers can guide you

2.) balance each half-reaction separately as follows:

- a) Balance coefficients for all atoms except H and O
- b) Add sufficient H_2O to side deficient in O to balance O
- c) Calculate the number of H atoms by which side is deficient
 - i) in acidic solution add H^+ to side deficient in H
 - ii) in basic solution add the # of H_2O to side deficient in H, and the same # of OH^- to other side
- d) Balance charges by adding e^- to side deficient in negative charge

- 3.) Multiply half reactions by suitable coefficients to balance the e^- and add the two half reactions together
- 4.) Cancel out species common to both sides of the equation
- 5.) Check both the atom and charge balance

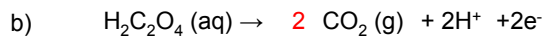


∴ Half reactions are:

- a) $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$
- b) $\text{H}_2\text{C}_2\text{O}_4 (\text{aq}) \rightarrow \text{CO}_2 (\text{g})$



Charge_{LHS} = $8 - 1 = +7$ Charge_{RHS} = $+2$ ∴ Add $5e^-$ to reactant side (reduction)

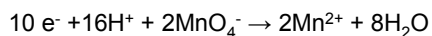


Charge_{LHS} = 0

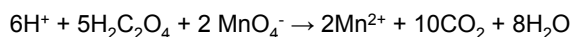
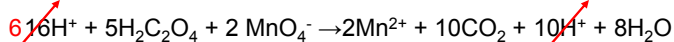
Charge_{RHS} = +2

- Products gain 2 e⁻;
- reactants oxidized

c) Multiply reduction reaction by x2 and the oxidation reaction by x 5 so that both reactions involve 10 e⁻



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Mass check: 2Mn, 28O, 10C and 16H on both sides

Charge_{LHS} = +6 - 2 = +4

Redox Reactions

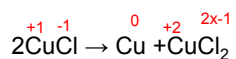
Charge_{RHS} = +4

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Disproportionation Reactions

For elements with 3 or more oxidation states, an element in an intermediate oxidation state can be both oxidized and reduced (a redox reaction known as disproportionation)

Example:



Here oxidation numbers help establish if redox reaction is also a disproportionation reaction

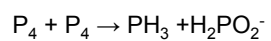
Such reactions can sometimes be difficult to balance

Example: Balance $\text{P}_4 \rightarrow \text{PH}_3 + \text{H}_2\text{PO}_2^-$ in basic solution

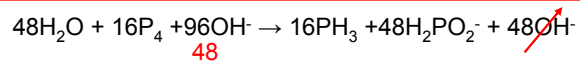
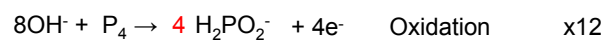
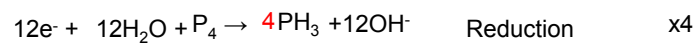
Hint Rewrite the equation with the disproportionating species written as reacting with itself

Redox Reactions

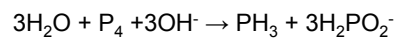
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Half reactions



Divide equation by 16



Mass check: 9H, 6O and 4 P on both sides of the equation

$$\text{Charge}_{\text{LHS}} = -3$$

$$\text{Charge}_{\text{RHS}} = -3$$

Balanced

Redox Reactions

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