Oxidation and Reduction

C020

A broad class of reactions in chemistry involves the exchange of electrons and are known as **red**uction-**ox**idation (redox) reactions

An atom is **oxidized** when it looses 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:

$Na \rightarrow Na^{+} + e^{-}$ $\quad$ $Fe^{2+} \rightarrow Fe^{3+} = e^{-}$

Examples of reduction half reactions:

$Cl_2 + 2e^{-} \rightarrow 2Cl^{-}$ $\quad$ $Cu^{2+} + 2e^{-} \rightarrow Cu$

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)

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

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)

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

Examples:

$\overset{+1}{H_2}\overset{-2}{O}$ Neutral = 0 = 2x(+1)-2

$\overset{+1}{H_2}\overset{-2?}{O_2}$ Neutral = 0= 2x(+1)+2x(-2) =-2

No problem. H has priority over O so solve for ON for O

Neutral = 0= 2x(+1)+2x(ON)

$\therefore$ ON = -1

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

$\overset{+1}{H_2}\overset{-2}{PO_4^-}$ Net charge = -1 = 2 x (+1) + ON(P) + 4 x (-2)

$\therefore$ 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

More examples

1) $\overset{+2}{Mg}\overset{-2}{O}$ Using ON(O) = -2

2) $\overset{-3}{P}\overset{3x(+1)}{H_3}$ Using ON(H) = +1

3) $\overset{+1}{H}\overset{-2}{S^-}$ Using ON(H) = +1 and ON(overall) = -1

(+1) + ON(S) = -1 $\therefore$ ON(S) = -2

4) $\overset{+5}{Cl}\overset{-2}{O_3^-}$ Using ON(O) = -2 which has higher priority over Cl

ON(Cl) + 3 x (-2) = -1 $\therefore$ ON(Cl) = +5

5) $\overset{+2}{S_2}\overset{-2}{O_3^{2-}}$ Using ON(O) = -2

2 x ON(S) + 3 x (-2) = -2 $\therefore$ 2 x ON(S) = +4

ON(S) = +2

6) $\overset{+1}{Na}\overset{-1}{Cl}$ Using ON(group I) = +1 and/or ON(group VII) = -1

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

Oxidation

Example:

+7 4x-2 2x+1 +3 4x-2 +2 +4 2X-2

$MnO_4^-(aq) + H_2C_2O_4(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$

Reduction

$\therefore$ Half reactions are:

a) $MnO_4^- \rightarrow Mn^{2+}$
b) $H_2C_2O_4(aq) \rightarrow CO_2\,(g)$

a) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

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

b) $H_2C_2O_4\ (aq) \rightarrow\ 2\ CO_2\ (g)\ + 2H^+\ + 2e^-$

Charge$_{LHS}$ = 0 Charge$_{RHS}$ = +2 $\therefore$ 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$^-$

$$10\ e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O$$

$$+$$

$$5H_2C_2O_4 \rightarrow 10CO_2 + 10H^+ + 10e^-$$

$$6\cancel{16}H^+ + 5H_2C_2O_4 + 2\ MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + \cancel{10H^+} + 8H_2O$$

$$\boxed{6H^+ + 5H_2C_2O_4 + 2\ MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O}$$

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

Charge$_{LHS}$ = +6 – 2 = +4 Charge$_{RHS}$ = +4

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 know as disproportionation)

Example:

$$2\overset{+1}{Cu}\overset{-1}{Cl} \rightarrow \overset{0}{Cu} + \overset{+2}{Cu}\overset{2x-1}{Cl_2}$$

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

Such reactions can sometimes be difficult to balance

Example: Balance $P_4 \rightarrow PH_3 + H_2PO_2^-$ in basic solution

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

$P_4 + P_4 \rightarrow PH_3 + H_2PO_2^-$

Half reactions

$12e^- + 12H_2O + P_4 \rightarrow 4PH_3 + 12OH^-$ Reduction x4

$8OH^- + P_4 \rightarrow 4\ H_2PO_2^- + 4e^-$ Oxidation x12

$48H_2O + 16P_4 + \underset{48}{96OH^-} \rightarrow 16PH_3 + 48H_2PO_2^- + \cancel{48OH^-}$

Divide equation by 16

$3H_2O + P_4 + 3OH^- \rightarrow PH_3 + 3H_2PO_2^-$

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

$Charge_{LHS} = -3$ $Charge_{RHS} = -3$

Balanced

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