REDOX – THE BASICS

Oxidation Numbers

- Assigning oxidation numbers to chemicals in a chemical reaction is simply a way of "account keeping" for electron transfer. The ***oxidation state*** or ***oxidation number*** of a chemical species gives us an indication of whether it has gained or lost electrons in a chemical reaction. As a result of redox reactions it is often the case that the charge of a species will change or at least the number of electrons that it has or shares will change.

- There are rules for assigning oxidation numbers. The RULES and the exceptions are listed below:

1. **The Ox N° of an element= 0**
   eg: Na, Mg, Cl_2, C, O_2, Ar, N_2.

2. **The Ox N° of a single ion = charge on the ion**
   eg: $Na^+ = +1$, $Cl^- = -1$, $O^{2-} = -2$.

3. **The Ox N° of all elements in a compound must add to ZERO**

   eg: *TOTAL Ox N°* (+2) (-4) (+2) = 0

   $$\begin{array}{ccc} (+2) & (-4) & (+2) = 0 \\ \uparrow & \uparrow & \nearrow \\ Mg & (O & H)_2 \\ \downarrow & \downarrow & \searrow \\ (+2) & (-2) & (+1) \end{array}$$

   INDIVIDUAL Ox N°: (+2) (-2) (+1)

   NB ❶: For the sake of consistency stick to the convention of putting individual states underneath the species and totals above, to assist in the mathematics.

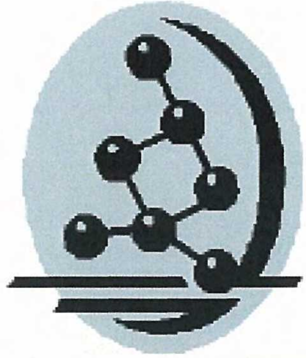
   NB ❷: The subscripts or indeed any balancing numbers in an equation **do not** alter the individual oxidation number of a species, only the TOTAL.

4. **The Ox N° of elements in a radical ion must add to the charge of that ion.**

   eg: *TOTAL Ox N°* (+12) (-14) = -2

   $$\begin{array}{cc} (+12) & (-14) = -2 \\ \uparrow & \nearrow \\ Cr_2 & O_7^{2-} \\ \downarrow & \searrow \\ (+6) & (-2) \end{array}$$

   INDIVIDUAL Ox N° (+6) (-2)



5. **The Ox N° of OXYGEN = -2**
   * Exception: Peroxides (H_2O_2/Na_2O_2) = -1

6. **The Ox N° of HYDROGEN = +1**
   * Exception: Hydrides (LiH, NaH) = -1

Using Oxidation Numbers

CHANGE OF OX STATE:

- When the Ox N° of an element **INCREASES** then it has undergone **OXIDATION**.
- When the Ox N° of an element **DECREASES** then it has undergone **REDUCTION**.
- You can identify if a reaction is REDOX by checking on the changes in Ox State.

- By simply checking the change in oxidation state, you can then tell whether or not oxidation and reduction have occurred. Reaction types other than redox (Acid/Base, Precipitation) will not result in changes in Ox N° of any species in the reaction. Not only can you tell this, but you can also tell at a glance the precise chemical that has been oxidised and that which has been reduced. This allows you to determine the oxidising and reducing agent.

EXAMPLE:

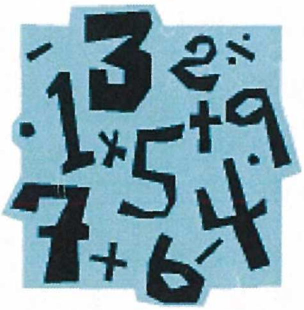
TOTAL Ox N°: (+2) (+7) (-8) = -1 (+1) (+3) (+2) (+2) (-2) =0

$$5\,Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5\,Fe^{3+} + Mn^{2+} + 4\,H_2O$$

INDIVIDUAL Ox N°: (+2) (+7) (-2) (+1) (+3) (+2) (+1) (-2)

Δ = +1 ∴ Oxidation

Δ = - 5 ∴ Reduction



- ➢ As Fe^{2+} ions have been oxidised, they must have acted as the ***Reducing Agent*** for this reaction.

- ➢ As Mn in MnO_4^- ions has been reduced the permanganate ion must have acted as the ***Oxidising Agent*** for this reaction.

NB: Despite the fact that it is only the **Mn** in **MnO_4^-** that has undergone a change in oxidation state, the whole chemical species is referred to as the Oxidising agent.

- If there is **no change** in oxidation number of anything in a reaction, then we can conclude that the process is not redox, this **does not mean** that there is **no reaction**!

(+2) (-1) (+2) (-2) = 0

$$Pb^{2+} + 2\,I^- \rightarrow PbI_2$$

(+2) (-1) (+2) (-1)

➲ This is a precipitation reaction rather than a redox reaction!

Common Oxidising and Reducing Agents

- Substances that are the most easily ***reduced*** are the best ***oxidisers***. They are found at the TOP LEFT of the reduction potential table.

  e.g. $\mathbf{F_2} + 2e^- \rightarrow 2F^-$
  $\mathbf{H_2O_2} + 2H^+ + 2e^- \rightarrow 2H_2O$
  $\mathbf{MnO_4^-} + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Other common Oxidisers ► $Cr_2O_7^{2-}$ (Dichromate ion), ClO^- (Hypochlorite ion) and H^+

- These substances are the best at taking in electrons or ***competing*** for electrons.

- The Standard Reduction Potential table really tells us what are the ***best competitors*** for electrons.

- Substances that are the most easily ***oxidised*** are the best ***reducers***. They are found at the BOTTOM RIGHT of the reduction potential table, as we read these equations in reverse when we are looking for oxidation processes.

  e.g. $K \rightarrow K^+ + e^-$
  $Ca \rightarrow Ca^{2+} + 2e^-$
  $Na \rightarrow Na^+ + e^-$

Other common Reducers ► C (Carbon), $C_2O_4^{2-}$ (Oxalate ion), H_2 Zn and Fe^{2+}

Environmental Oxidation

► Oxygen (O_2) is probably the most common environmental Oxidising Agent as it is plentiful in the atmosphere. Oxygen is capable of gaining four electrons per molecule and in being reduced causes the oxidation of other species. Combustion is a rapid form of this oxidation while corrosion is a much slower one.

$$\mathbf{O_2 + 4e^- \rightarrow 2O^{2-}}$$

- The half equation for the reduction of oxygen above does not appear in the standard reduction potential table because the reactions in this table are in aqueous phase. Experience will tell us when an oxidation reaction with oxygen is fast or slow and this will very much depend on the reaction conditions and consequent amount of available ***activation energy***.