Oxidation-Reduction (Redox) Reactions

Oxidation-Reduction (Redox) reactions are electron transfer reactions which are considered to be a part of everyday life. They range from the burning of fossil fuel to the action of house-hold bleach. Also, most metallic and non-metallic elements are obtained from their ores by either oxidation or reduction reactions. Many (but not all) important redox reactions take place in aqueous systems.

Oxidation reaction: Half-reaction that refers to loss of electron/electrons

$$Ca \rightarrow Ca^{2+} + 2e^{-}$$

Reduction reaction: Half-reaction that refers to gain of electron/electrons

$$O + 2e^{-} \rightarrow O^{2-}$$

In the formation of CaO, Ca is oxidized, and itself acts as a reducing agent by giving up electrons, while oxygen is reduced, and itself acts as an oxidizing agent by accepting electrons.

Let us consider another example in the next page:

Example 1*:* When metallic zinc is added to a solution containing copper (II) sulfate ($CuSO_4$) the blue colour of the solution disappears due to the following redox reaction*:*

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

The oxidation and reduction half-reactions are *:*

Oxidation reaction: $Zn(s) \rightarrow Zn^{2+}(s) + 2e^{-}$

Reduction reaction: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Problem*:* Metallic copper reduces silver ions in a solution of $AgNO_3$. Write the half-reactions for redox reactions.

❖ The definition of oxidation and reduction in terms of electron transfer can be applied for **ionic compounds** only. It cannot, however, be applied for the formation of molecular compounds like HCl and SO_2 (covalent compounds). Let us consider the reactions*:*

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

These reactions are considered as redox reactions, because experiments show that there is partial transfer of electrons from H to Cl in HCl and from S to O in SO_2. It is, therefore, convenient to define oxidation and reduction in terms of *Oxidation Number*.

Oxidation Number (ON)

It is the number charge assigned on an element or a species (elements, ions or molecules) during its loss or gain of electron.

- For the loss of an electron = a positive Oxidation Number (ON) is obtained

$$Na(g) \rightarrow Na^{+}(g) + e^{-}$$

- For the gain of an electron = a negative ON is obtained

$$Cl\,(g) + e^{-} \rightarrow Cl^{-}(g)$$

$$\overset{0}{H_2}(g) + \overset{0}{Cl_2}(g) \rightarrow 2\,\overset{+1}{H}\overset{-1}{Cl}(g) \qquad (01)$$

$$\overset{0}{S}(g) + \overset{0}{O_2}(g) \rightarrow \overset{+4}{S}\overset{-2}{O_2}(g) \qquad (02)$$

The numbers above the element symbols are the oxidation numbers. As can be seen in both the reactions the charges on the atoms on the reactant molecules are zero. On the other hand it is assumed that complete transfer (*loss or gain*) of electron have taken place on the atoms in the product molecules. The oxidation number (ON) reflects the number of electrons transferred.

Oxidation: An increase of ON indicates oxidation. Hydrogen and sulfur in reactions (01) and (02) have been oxidized.

Reduction: Decrease of ON indicates reduction. Chlorine and oxygen in reactions (01) and (02) have been reduced.

Remember- the sum of ON of the atoms in a molecule is always zero, because the molecule as a whole is neutral.

❖ Rules of assigning Oxidation Number (ON) to elements

Oxidation numbers are bookkeeping numbers. They allow chemists to do things such as balance redox (reduction/oxidation) equations. Oxidation numbers are positive or negative numbers, but don’t confuse them with positive or negative charges on ions or valences.

Oxidation numbers are assigned to elements using these rules:

Rule 1: The oxidation number of an element in its free (uncombined) state is zero — for example, Al(s) or Zn(s). This is also true for elements found in nature as diatomic (two-atom) elements H_2, O_2, N_2, Cl_2, Br_2

Rule 2: The oxidation number of a monatomic (one-atom) ion is the same as the charge on the ion, for example:

$$Na^{+1} = +1,\ S^{2-} = -2$$

Rule 3: The sum of all oxidation numbers in a neutral compound is zero. The sum of all oxidation numbers in a polyatomic (many-atom) ion is equal to the charge on the ion. This rule often allows chemists to calculate the oxidation number of an atom that may have multiple oxidation states, if the other atoms in the ion have known oxidation numbers.

Rule 4: The oxidation number of an alkali metal (IA family) in a compound is +1; the oxidation number of an alkaline earth metal (IIA family) in a compound is +2.

Rule 5: The oxidation number of oxygen in a compound is usually –2. If, however, the oxygen is in a class of compounds called peroxides (for example, hydrogen peroxide), then the oxygen has an oxidation number of –1. If the oxygen is bonded to fluorine, the number is +1.

Rule 6: The oxidation state of hydrogen in a compound is usually +1. If the hydrogen is part of a binary metal hydride (compound of hydrogen and some metal like LiH, NaH, CaH_2), then the oxidation state of hydrogen is –1.

Rule 7: The oxidation number of fluorine is always –1. Chlorine, bromine, and iodine usually have an oxidation number of –1, unless they're in combination with an oxygen or fluorine.

TASK: Assign ON to all the elements in the following compounds and ion:

(i) Li_2O, (ii) HNO_3, (iii) $Cr_2O_7^{2-}$ (iv) MnO_4^-

Disproportionation is a chemical reaction, typically a redox reaction, where a molecule is transformed into two or more dissimilar products. In a redox reaction, the species is simultaneously oxidized and reduced to form at least two different products.

Consider the following skeleton reaction which takes place in *acidic medium*:

$$\overset{+7}{Mn}O_4^- \ (aq) + \overset{+2}{Fe}{}^{2+}(aq) \rightarrow \overset{+2}{Mn}{}^{2+}(aq) + \overset{+3}{Fe}{}^{3+}(aq)$$

In this reaction MnO_4^- (purple color) acts as an oxidizing agent in acidic solution and itself is reduced to Mn^{2+} (pale pink to colorless). Iron (II) (pale green) is oxidized to Fe^{3+} (pale yellow to colorless).

Oxidising agents

- are electron rich species

- oxidized other but reduced itself

Example: All non- metals (except inert gas), F_2, Cl_2, Br_2, I_2, O_2, HNO_3, Conc.H_2SO_4, $KMnO_4$, $K_2Cr_2O_7$, etc

$$Cl_2\ (g) \rightarrow 2Cl\ (g)$$

$$Cl\ (g) + e^- \rightarrow Cl^-(g)$$

Reducing agents

- are electron-deficient species

- oxidized itself but reduced other

Example: All metals, Hydrogen, carbon, CO, H_2S, SO_2, Oxalic acid ($H_2C_2O_4$), $SnCl_2$.