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Oxidation-Reduction reactions

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Classical Concept

Oxidation simply means the addition of oxygen to elements or compounds. The reduction is the removal of oxygen from a compounds.

Addition of oxygen: $2Mg + O_2 \rightarrow 2MgO$

Removal of oxygen: $2CuO \rightarrow 2Cu + O_2$

Valence state concept

Oxidation is a chemical reaction which involves change of valence state in the positive direction.

$FeCl_2 + Cl_2 \rightarrow FeCl_3$

Reduction is a chemical reaction which involves change of valence state in the negative direction.

$FeCl_3 \rightarrow FeCl_2 + Cl_2$

$Cl_2 + 2e \rightarrow 2Cl^-$

Electronic concept

Oxidation Reaction

Oxidation is the loss of electrons or an increase in the oxidation state of an atom, an ion, or of certain atoms in a molecule.

$M \rightarrow M^{+} + e^{-}$ (loss of electron)- Oxidation

Reduction Reaction

Reduction is the gain of electrons or a decrease in the oxidation state of an atom, an ion, or of certain atoms in a molecule (a reduction in oxidation state).

$X + e^{-} \rightarrow X^{-}$ (gain of electron)- Reduction

Oxidizing Agent or Oxidant

An oxidizing agent is one that accepts electrons and is thereby reduced. Here in the following reaction, Cu^{2+} is an oxidizing agent and it is reduced because Cu^{2+} accepts two electron from Fe.

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

Reducing Agent or Reductant

A reducing agent is one that gives off electrons and is thereby oxidized. In the upper reaction, Fe is a reducing agent and it is oxidized because Fe° donate two electrons to Cu^{2+}.

Oxidation state and Oxidation number

The oxidation number (or oxidation state) of an atom in a substance as the actual charge (+ve or –ve or zero) of the atom if it exists as a monoatomic ion, or a hypothetical charge assigned to the atom in the substance by simple rule.

$$Mg^{\circ} + Cl_2^{\circ} = Mg^{2+}Cl^{-}Cl^{-}$$

The oxidation number of Mg undergoes a change from zero in the free state to 2+ and the oxidation number of chlorine changes from zero in the free state to 1-. Neutral molecule has zero charge e.g. $(MgCl_2)^{\circ}$

Rules for Assigning Oxidation Numbers

(i) The convention is that the cation is written first in a formula, followed by the anion. For example, in NaH, the H is H^- (hydride ion) in HCl, the H is H^+ (hydrogen ion).

(ii)The oxidation number of a free element is always 0. The atoms in He and N_2, for example, have oxidation numbers of 0.

(iii) The oxidation number of a monatomic ion equals the charge of the ion. For example, the oxidation number of Na^+ is 1+; the oxidation number of N^{3-} is 3-.

(iv) The usual oxidation number of hydrogen is 1+. The oxidation number of hydrogen is 1- in compounds containing elements that are less electronegative than hydrogen, as in CaH_2.
(v) The oxidation number of oxygen in compounds is usually 2-. Exceptions include OF_2 because F is more electronegative than O, and BaO_2, due to the structure of the peroxide ion, which is $[O\text{-}O]^{2-}$.
(vi)The oxidation number of a Group IA element in a compound is 1+.
(vii) The oxidation number of a Group IIA element in a compound is 2+.

(viii) The oxidation number of a Group VIIA element in a compound is 1-, except when that element is combined with one having a higher Electronegativity. The oxidation number of Cl is 1- in HCl, but the oxidation number of Cl is 1+ in HOCl.

(ix) The sum of the oxidation numbers of all of the atoms in a neutral compound is 0. e.g. $(MgCl_2)^\circ$.

(x) The sum of the oxidation numbers in a polyatomic ion is equal to the charge of the ion. For example, the sum of the oxidation numbers for SO_4^{2-} is 2-.

The Half-Reaction Method of Balancing Redox Equations

A powerful technique for balancing oxidation-reduction equations involves dividing these reactions into separate oxidation and reduction half-reactions. We then balance the half-reactions, one at a time, and combine them so that electrons are neither created nor destroyed in the reaction. The steps are-

Step 1: Assign oxidation numbers to atoms on both sides of the equation.

Step 2: Write a skeleton equation for the reaction.

Step 3: Determine which atoms are oxidized and which are reduced.

Step 4: Divide the reaction into oxidation and reduction half-reactions and balance these half-reactions one at a time.

Step 5: Complete and balance each half-reaction:

(a) Balance all atoms except O and H.

(b) Balance O atoms by adding H_2O's to one side of the equation

(c) Balance H atoms by adding H^+ ions to one side of equation

(d) Balance electronic charge by adding e to more positive side.

Step 6: Combine these half-reactions so that electrons are neither created nor destroyed.
Step 7: Balance the remainder of the equation by inspection, if necessary.

Example 1: Ferrous chloride is oxidized by chlorine to ferric chloride.
Skeleton reaction
$FeCl_2 + Cl_2 = FeCl_3$

Two half reactions:
$Cl_2^{\circ} + 2e = 2Cl^-$ (reduction)…….(1)
$Fe^{2+}Cl^-Cl^- = Fe^{3+}2Cl^- + e$ (oxidation)……..(2)

Since the loss and gain of electrons during the process must be equal, the second part has to be multiplied by 2.

$Cl_2 + 2e = 2Cl^-$

$2FeCl_2 = 2Fe^{3+}4Cl^- + 2e$

Full reaction: $2FeCl_2 + Cl_2 = 2FeCl_3$

Example 2: H_2S is oxidized to H_2SO_4 when passed into a concentrated aq. solution of bromine.

Skeleton reaction:

$Br_2 + H_2S + H_2O \rightarrow H_2SO_4 + HBr$

Two half reactions:

$Br_2^{\circ} + 2e = 2Br^-$ (reduction)

$H_2S^{2-} + 4H_2O = H_2S^{6+}O_4 + 8H^+ + 8e$ (oxidation)

The loss and gain of electrons must be equal. Hence the upper half-reaction is to be multiplied by 4.

$4Br_2 + 8e = 8Br^-$

$H_2S + 4H_2O = H_2SO_4 + 8H^+ + 8e$

Full reaction: $4Br_2 + H_2S + 4H_2O = H_2SO_4 + 8HBr$

Example 3: Potassium dichromate oxidizes potassium iodide in acidic solution liberating iodine.

Skeleton reaction

$K_2Cr_2O_7 + KI + H^+ \rightarrow 2Cr^{3+} + 2K^+ + H_2O + I_2$

The half-reactions are

$K_2{}^{2+}Cr_2{}^{12+}O_7 + 6e = 2Cr^{3+} + 2K^+ + 7O^{2-}$ (reduction)

$2KI = I_2 + 2K^+ + 2e$ (oxidation)

Now, $7O^{2-}$ require $14H^+$ ions to form $7H_2O$, therefore, $14H^+$ is to introduced in the half-reaction and in order to make the number of electron lost and gained equal, the half-reactions is to be multiplied by 3.

$K_2{}^{2+}Cr_2{}^{12+}O_7 + 6e = 2Cr^{3+} + 2K^+ + 7O^{2-}$

$7O^{2-} + 14H^+ = 7H_2O$

$6KI = 3I_2 + 6K^+ + 6e$

Overall equation:

$K_2Cr_2O_7 + 6KI + 14H^+ \rightarrow 2Cr^{3+} + 8K^+ + 7H_2O + 3I_2$

H^+ can come from any acid (HCl, H_2SO_4 etc.)

$K_2Cr_2O_7 + 6KI + 14HCl \rightarrow 2CrCl_3 + 8KCl + 7H_2O + 3I_2$

Example 4: Potassium permanganate oxidizes H_2S in aq. solution and shulphur is liberated.

Skeleton reaction:

$KMnO_4 + H_2S + H^+ \rightarrow K^+ + Mn^{2+} + S + H_2O$

Half-reactions are

$K^+Mn^{7+}O_4 + 5e = K^+ + Mn^{2+} + 4O^{2-}$ (reduction) (1)

$4O^{2-} + 8H^+ = 4H_2O$

$H_2S^{2-} = 2H^+ + S° + 2e$ (oxidation) ….(2)

Multiplying eqn. (1) by 2 and eqn. (2) by 5 in order to make the loss and gain of electrons equal.

$2K^+Mn^{7+}O_4 + 10e = 2K^+ + 2Mn^{2+} + 8O^{2-}$

$8O^{2-} + 16H^+ = 8H_2O$

$5H_2S^{2-} = 10H^+ + 5S° + 10e$

Overall reaction:

$2KMnO_4 + 5H_2S + 6H^+ = 2K^+ + 2Mn^{2+} + 5S + 8H_2O$

If H_2SO_4 is added-

$2KMnO_4 + 5H_2S + 3H_2SO_4 = 2K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$

Example 5: The oxidation of sodium thiosulphate by iodine.

The skeleton reaction:

$Na_2S_2O_3 + I_2 = Na_2S_4O_6 + NaI$

$Na_2S_2O_3$ is converted to $Na_2S_4O_6$, I_2 is converted to I^-.

Here $Na_2S_2^{4+}O_3 = Na_2S_4^{10+}O6$

Thus each S atom of thiosulphate loses ½ electron for oxidation to tetrathionate ($S_4O_6^{2-}$). 4S atoms in tetrathionate must come from 2 molecules of thiosulphate ($S_2O_3^{2-}$). Hence, the total change in oxidation number of S is from 2(+4)=+8 to 4 x 2½=+10

$2Na_2S_2^{8+}O_3 = Na_2S_4^{10+}O_6 + 2Na^+ + 2e$ (oxidation)

$I_2 + 2e = 2I^-$ (reduction)

Overall reaction:

$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$