

Review: Redox Reactions

Redox reactions involve electron transfer

Definition: OIL- Oxidation Is Loss of electrons
RIG- Reduction Is Gain of electrons

Oxidation Numbers:

A form of book-keeping for electrons, enables us to keep track of electrons. An oxidation number is made up of two parts:

i) the sign: if the sign is: **+positive the atom has lost control of its e⁻s**
 -negative the atom as gained control of its e⁻s

ii) the **number** is always written as a Roman Number, this gives the number of electrons over which electron control has changed compared to the situation in the pure element.

Rules for Working out Oxidation Numbers

1. Elements = 0
2. Oxygen = -2 (except peroxides +1)
3. H = -1 (except metal hydrides -1)
4. ion = charge on ion
5. Sum of oxidation numbers of all atoms in a compound = 0
6. Sum of oxidation numbers of all atoms in an ion = charge on the ion

Recognizing Redox Equations

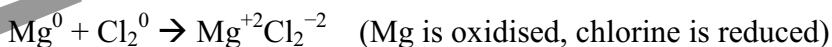
Redox Equations are recognised by the following steps:

- i) work out the Oxidation numbers of all atoms in the equation
- ii) and then seeing if the oxidation number of any atom has a changed.

Therefore a redox reaction has taken place.

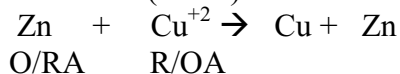
↑ increase in oxidation number = Oxidation
↓ decrease in oxidation number = Reduction

Example 1:



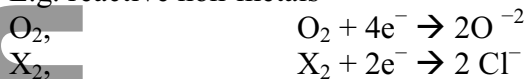
Redox is a 2-way Process:

Reduction and Oxidation (redox) occur simultaneously.

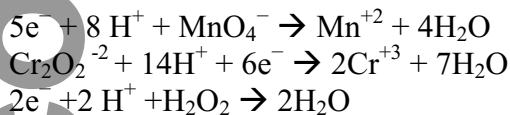


Oxidising agents [aka: oxidants]: cause oxidation in other reacting species, makes other reacting substances lose electrons. The oxidant gains electrons, i.e. is an **electron acceptor**, (recall: Lewis Acid); however an oxidant is itself reduced.

E.g. reactive non-metals

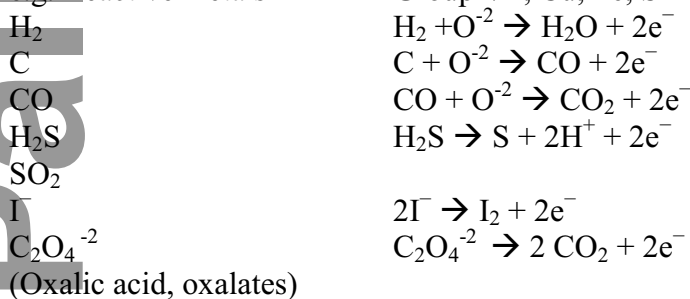


Oxo-compounds: $\text{KMnO}_4 / \text{H}^+$ $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}^+$, H_2O_2



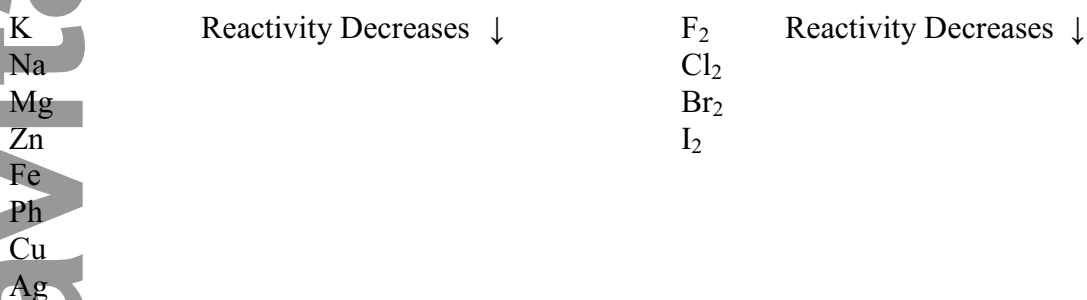
Reducing Agents: cause reduction in other substances; makes reacting species gain electrons. [aka: Reductant] Loses e^- / e^- donors.

e.g. Reactive metals



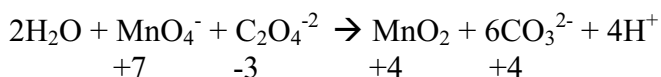
Order of Reacting for Metals and Non-metals

Reacting Series/ Electrochemical series



Balancing Redox Equations using oxidation numbers

1. Assign O.N to all atoms in the Equation
2. Determine which elements undergo oxidation/reduction
3. Balance each change in O.N with a coefficient
4. Balance the rest by inspection:



Balancing ½ electron method in Acid/Base medium

1. Divide equation into two ½ equation: an oxidation and a reduction
2. Balance all other atoms other than H/O
3. Balance O using H₂O
4. Balance H using H⁺
5. Balance charges using e⁻s
6. Balance e⁻s using multiplication factor (in both equations)
7. Add the two ½ equations.
- 8.

[Easy way to remember this: My Wallaby Hurls Eggs
 Mass Water Hydrogen Electrons]

Example: balance the following in acid medium: $\text{MnO}_4^{-1} + \text{H}_2\text{O}_2 \rightarrow \text{Mn}^{2+} + \text{O}_2$

Standard Electrode Potentials, E°

These are relative values. They are always compared to the Hydrogen Electrode Potential

Definition: E° is defined as the potential difference between a standard half-cell and the standard hydrogen half-cell. Note: the hydrogen half-cell has an electrode potential of zero and an equation is : $\text{H}^{+1} + \text{e}^{-} \rightarrow \frac{1}{2} \text{H}_2$

There are three types of Half-Cells:

1. metal dipping into a solution of its ions, Zn / Zn²⁺
2. a gas in contact with an inert electrode
3. An inert metal in contact with a solution containing ions in two different oxidation states, e.g. Pt_(s) | Fe / Fe²⁺

[In the drawing of an electrochemical cell, remember to use an inert electrode for gases and ion/ion solutions; example for the hydrogen half-cell: Pt_(s) | H_{2(g)}, | H⁺_(aq) (1.0)mol/L]

Cell Notation:

Anode | anode electrolyte || cathode electrolyte |cathode

Factors Affecting E°

E° is an intensive property, i.e. it is independent of the physical dimensions of the cell.

A change in conditions produces a change in electrode potential.

They will be changed by

1. Pressure of gases
2. Temperature
3. Concentrations of ions
4. pH of solutions
5. ligands present

How to Predict whether a redox rxn will happen, i.e. spontaneous or non-spontaneous?

1. The bigger E° , i.e. the more positive value will proceed in the direction \rightarrow
The lower E° will have to be reversed, i.e. \leftarrow
2. Multiply each of the equations by 'n' to balance electrons in both equations, but **do not** multiply the E° value by the factor 'n'
3. Add the 2 equations
4. If the E° determined for the overall equation is **positive**, then the reaction will occur = **spontaneous** (> 0.4)
If the determined overall E° is **negative**, then the reaction will not occur \rightarrow **non-spontaneous**

E° positive: products predominant

The feasibility of a Rxn:

Standard free energy change ΔG° must be negative for a chemical reaction to occur.

$$\Delta G^\circ = -nFE^\circ$$

n= number of electrons transferred

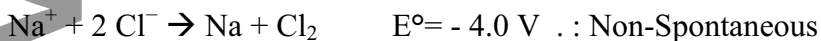
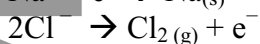
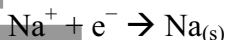
F= Faradays constant = 964951

E° = electrode potential value

For a reaction to be feasible: $E^\circ = \text{positive}$
 $\Delta G^\circ = \text{negative}$

Property	ΔG°	E°
Spontaneous (ECC)	-	+
Non-spontaneous	+	-
Equilibrium	0	0

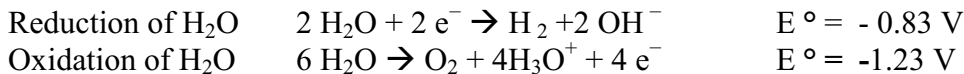
Electrolysis



Summary

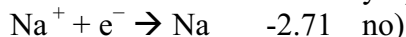
Cell Type	Electrode	Function	Polarity of electrode
Electrochemical Cell (battery)	Anode	oxidation	-
	Cathode	reduction	+
Electrolysis	Anode	oxidation	+
	Cathode	reduction	-

Electrolysis of Aqueous Solution



Generally:

1. if a substance has a reduction potential less negative (i.e. more +ve) than -0.83V (for H₂O) then the substance will be reduced (e.g. $\text{Cu}^{+2} + 2 \text{e}^- \rightarrow \text{Cu}$ +0.34 yes)



2. Metals higher in the electrochemical series are difficult to reduce in aqueous solution

3. Metals lower down in the electrochemical series are discharged preferentially

4. Order of discharge of ions: $\text{SO}_4^{-2} \rightarrow \text{NO}_3 \rightarrow \text{Cl}^- \rightarrow \text{OH}^- \rightarrow \text{Br}^- \rightarrow \text{I}^-$
→ increasing tendency to discharge

5. Concentration of solution H₂ or Cl₂ oxidation: $\text{H}_2\text{O} \rightarrow \text{O}_2$ -1.23

e.g. Dilute NaCl / concentration NaCl (i.e.Brine) $\text{Cl}^- \rightarrow \text{Cl}_2$ $\frac{-1.36}{0.03\text{V}}$

Effect of Electrodes on Electrolysis

Products of electrolysis also depend on the nature of electrode. Consider the electrolysis of copper (II) chloride solution:

		Cathode	Anode
$\text{CuCl}_{2(\text{aq})}$	Inert electrode	$\text{Cu}_{(\text{s})}$	Cl_2/O_2
	Cu Electrodes	Cu	Cu anode dissolves

Quantitative Aspects of Electrolytic Cells

Current Amp (I) = $\frac{\text{Electric charge (coulombs, C)}}{\text{Time (seconds, s)}}$

$$C = I \cdot t$$

Faraday Constant: Charge carried by 1 mol of electrons = 96485 C/ mol

$$\frac{1 \text{ mol e}^-}{n \text{ mol e}^-} = \frac{96485 \text{ C (1F)}}{C}$$

Coulombs = n mol e⁻ (96485 → 1F)

Or

$$\text{Number of mol e}^- = \frac{\text{coulombs}}{\text{Faraday}} = \frac{C}{F}$$

$$(n = C/F)$$

Ex: What mass of Cr is deposited when a current of 2.05 A is passed for 1.00 h through a solution of chromium (III) sulphate?

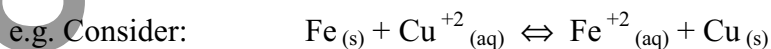
Nernst Equation

The Nernst Equation gives the variation of electrode potential with concentration.

$$E = E^\circ - \frac{RT}{nF} \ln Q \qquad Q = \text{Reaction Quotient} \qquad \text{ratio of: } \frac{[\text{Prod}]}{[\text{React}]}$$

At 25°C, T= 298K, R= 8.314 kJ , F= 96 485 C/mol

$$E = E^\circ - \frac{0.0257}{n} \ln Q \qquad (\text{or } E^\circ - \frac{0.0592}{n} \log Q)$$



If the concentration of Cu^{+2} increased, $[\text{Cu}^{+2}] \uparrow$
Then, the forward reaction will be favoured, thus increasing the electrode potential, $E \uparrow$

If the concentration of $[\text{Fe}^{+2}]$ is increased, the reverse reaction is favoured, thus decreasing the value of the electrode potential.

Nernst Equation and the Equilibrium Constant

At Equilibrium, $E = 0$

$$0 = E^\circ - \frac{0.0257}{n} \ln Q \qquad (Q \text{ refers to the equilibrium constant, } K)$$

$$0 = E^\circ - \frac{0.0257}{n} \ln K$$

$$\ln K = \frac{nE^\circ}{0.0257}$$

$$K = e^{\frac{nE^\circ}{0.0257}}$$