Review: Redox Reactions

Redox reactions involve electron transfer

Definition: OIL- **O**xidation **I**s **L**oss of electrons
RIG- **R**eduction **I**s **G**ain 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 (expect 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:

$Mg^0 + Cl_2^0 \rightarrow Mg^{+2}Cl_2^{-2}$ (Mg is oxidised, chlorine is reduced)

$S^{+4}O_2^{-2} + H_2^{+1}S^{-2} \rightarrow S^0 + H_2^{+1}O^{-2}$ (S in SO_2 is reduced and S in H_2S is oxidized)

Redox is a 2-way Process:
Reduction and Oxidation (redox) occur simultaneously.

$Zn + Cu^{+2} \rightarrow Cu + Zn$
O/RA R/OA

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

O_2,	$O_2 + 4e^- \rightarrow 2O^{-2}$
X_2,	$X_2 + 2e^- \rightarrow 2\,Cl^-$

Oxo-compounds: $KMnO_4 / H^+$ $K_2Cr_2O_2 / H^+$, H_2O_2 .

$5e^- + 8\,H^+ + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$
$Cr_2O_2^{-2} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$
$2e^- + 2\,H^+ + H_2O_2 \rightarrow 2H_2O$

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

e.g. Reactive metals	Group I/II, Cu, Fe, Sn	$M \rightarrow M^{n+} + ne^-$
H_2	$H_2 + O^{-2} \rightarrow H_2O + 2e^-$	
C	$C + O^{-2} \rightarrow CO + 2e^-$	
CO	$CO + O^{-2} \rightarrow CO_2 + 2e^-$	
H_2S	$H_2S \rightarrow S + 2H^+ + 2e^-$	
SO_2		
I^-	$2I^- \rightarrow I_2 + 2e^-$	
$C_2O_4^{-2}$ (Oxalic acid, oxalates)	$C_2O_4^{-2} \rightarrow 2\,CO_2 + 2e^-$	

Order of Reacting for Metals and Non-metals

Reacting Series/ Electrochemical series

K	Reactivity Decreases ↓	F_2	Reactivity Decreases ↓
Na		Cl_2	
Mg		Br_2	
Zn		I_2	
Fe			
Ph			
Cu			
Ag			

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:

$2H_2O + MnO_4^- + C_2O_4^{-2} \rightarrow MnO_2 + 6CO_3^{2-} + 4H^+$
+7 -3 +4 +4

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 H_2O
4. Balance H using H^+
5. Balance changes 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: **M**y **W**allaby **H**urls **E**ggs
Mass **W**ater **H**ydgrogen **E**lectrons]

Example: balance the following in acid medium: $MnO_4^{-1} + H_2O_2 \rightarrow Mn^{2+} + O_2$

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 : $H^{+1} + e^- \rightarrow \frac{1}{2} H_2$

There are three types of Half-Cells:
1.metal dipping into a solution of its ions, Zn / Zn^{2+}
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. $Pt_{(s)} | Fe / Fe^{2+}$

[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 charge 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 →
   The lower E° will have to be reversed, i.e. ←
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 → **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.

$$\Delta G° = -nFE°$$

n= number of electrons transferred
F= Faradays constant = 964951
E° = electrode potential value

For a reaction to be feasible: E° = positive
ΔG° = negative

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

Electrolysis

$Na^+ + e^- \rightarrow Na_{(s)}$
$2Cl^- \rightarrow Cl_{2\,(g)} + e^-$

$Na^+ + 2\,Cl^- \rightarrow Na + Cl_2$ E°= - 4.0 V . : Non-Spontaneous

Summary

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

Electrolysis of Aqueous Solution

Reduction of H_2O	$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$	$E° = -0.83$ V
Oxidation of H_2O	$6\,H_2O \rightarrow O_2 + 4H_3O^+ + 4\,e^-$	$E° = -1.23$ V

Generally:

1. if a substance has a reduction potential less negative (i.e. more +ve) than -0.83V (for H_2O) then the substance will be reduced (e.g. $Cu^{+2} + 2\,e^- \rightarrow Cu$ +0.34 yes)
   $Na^+ + e^- \rightarrow Na$ -2.71 no)
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: $SO_4^{-2} \rightarrow NO_3 \rightarrow Cl^- \rightarrow OH^- \rightarrow Br^- \rightarrow I^-$
   $\rightarrow$ increasing tendency to discharge
5. Concentration of solution H_2 or Cl_2 oxidation: $H_2O \rightarrow O_2$ -1.23
   e.g. Dilute NaCl / concentration NaCl (i.e.Brine) $Cl^- \rightarrow Cl_2$ -1.36
   0.03V

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**
$CuCl_{2(aq)}$	Inert electrode	$Cu_{(s)}$	Cl_2/O_2
	Cu Electrodes	Cu	Cu anode dissolves

Quantitative Aspects of Electrolytic Cells

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

$$C = I\cdot t$$

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

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

Coulombs= n mol e^- (96485 $\rightarrow$ 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.

$$E = E° - \frac{RT}{nF} \ln Q$$

Q = Reaction Quotient ratio of: $\frac{[Prod]}{[React]}$

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

$$E = E° - \frac{0.0257}{n} \ln Q \qquad \left(\text{or } E° - \frac{0.0592}{n} \log Q\right)$$

e.g. Consider: $Fe_{(s)} + Cu^{+2}_{(aq)} \Leftrightarrow Fe^{+2}_{(aq)} + Cu_{(s)}$

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

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

Nernst Equation and the Equilibrium Constant

At Equilibrium, E = 0

$$0 = E° - \frac{0.257}{n} \ln Q$$

(Q refers to the equilibrium constant,K)

$$0 = E° - \frac{0.0257}{n} \ln K$$

$$\ln K = \frac{nE°}{0.0257}$$

$$\mathbf{K = e^{\frac{nE°}{0.0257}}}$$