

CHM 101

Redox reactions and Electrochemistry

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Redox Reactions (Oxidation – reduction reaction)

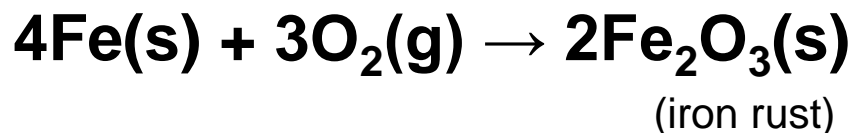
- ❖ Keep us alive (photosynthesis; muscle operation)
- ❖ Recover metals from ores
- ❖ Convert petroleum into petrochemicals & pharmaceuticals
- ❖ Generate electricity
- ❖ Power CD's, portable computers, cell phones

BUT CAN ALSO DESTROY CORROSION

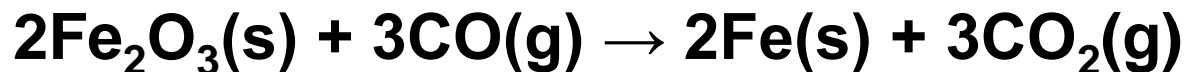
Redox Reactions

Definition in terms of oxygen:

Oxidation = addition of O₂ to a substance (element or compound) e.g. rusting of iron nails due to exposure to oxygen;



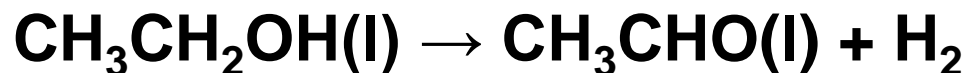
Reduction = Removal of O₂ from a compound e.g. production of iron from iron-ore i.e. reduction of iron ore or iron oxide



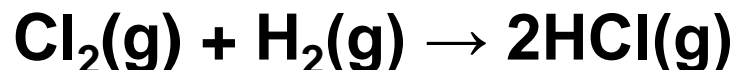
Redox Reactions

Definition in terms of hydrogen:

Oxidation = removal of hydrogen from a compound

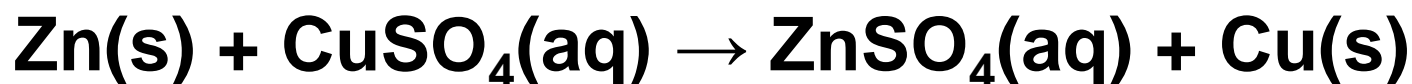


Reduction = addition of H_2 to an element or a compound



Redox Reactions

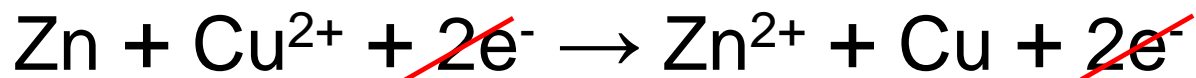
- Definition in terms of oxidation number
- Consider the reaction:



- (1) $\text{Zn}^0 \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (2) $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0$
- (1) and (2) are called '**half-reactions**'

Redox Reactions

- The overall equation can be obtained by adding the two '**half-reactions**' together, so that the electrons cancel out on each side:



- The overall equation is



Redox Reactions

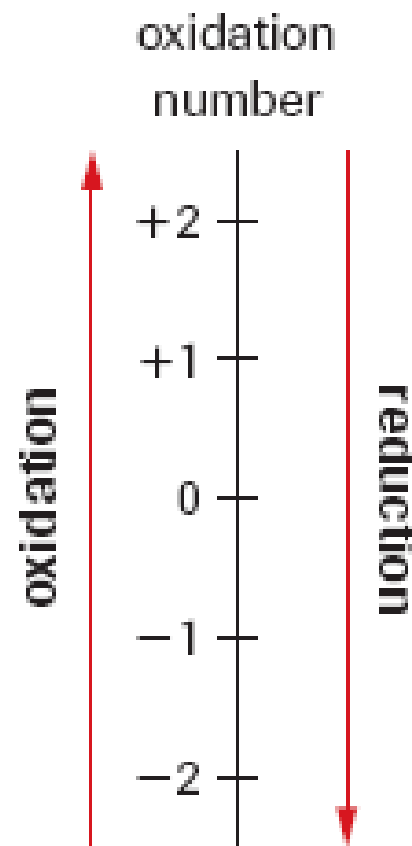
- **Oxidation:** in half-reaction (1), oxidation number of Zinc increases from 0 to +2, i.e.
 - (a) increase in oxidation number OR
 - (b) Zn atom **loses** 2 electrons to become zinc ion.

* This process is termed **oxidation** and we say that Zn is oxidized to Zn^{2+}
 - **Reduction:** in half-reaction (2), oxidation number of copper decreases from +2 to 0 i.e.
 - (a) decrease in oxidation number OR
 - (b) the copper atom **gains** two electrons from the zinc atom.

* This process is termed **reduction** and we say that Cu ion is reduced
- Therefore, **oxidation** occurs when electrons are lost,
reduction occurs when electrons are gained.

Redox Reactions in terms of O.N.

- **Oxidation** is an increase in the oxidation number.
- **Reduction** is a decrease in the oxidation number.
- An ***oxidizing agent*** is a substance which brings about the **oxidation of another substance**. In the process, it is itself reduced; **Cu salt**
- A **reducing agent** is a specie which brings about the **reduction of another substance**. In the process, it is itself oxidized; **Zn**.



Example

- Do example from print out to know half reactions (oxidation/reduction), overall reaction, spectator ions

Key points: Redox reactions

- Oxidation (electron loss) and reduction (electron gain) must always occur together.
- Electrons given up in the oxidation half-reaction are taken up in the reduction half-reaction (electrons in both half reactions are equal. Therefore, the overall reaction is independent of electrons.
- The overall reaction must be balanced in terms of matter and charge, [law of conservation of mass].

Oxidation Numbers (O.N.)

- Definition: The oxidation number or oxidation state of an atom is a positive or negative number which is decided using agreed rules.
- We assign a *formal* “+” charge to the H and call it H^+ , and a *formal* “-” charge to Cl and call it Cl^- .
- *Note that these are not real charges, and UNLIKE those of ions in aqueous solution, can not be measured experimentally
- Now H^+ has O.N. of +1, and Cl^- has an O.N of -1.



Rules for Assigning an Oxidation Number (O.N.)

General rules

1. For an atom in its elemental form (uncombined) (Na, O₂, Cl₂, etc.): O.N. = 0
2. For a monoatomic ion (e.g. Cu²⁺ / O₂⁻): O.N. = ion charge (+2,Cu or -1,O
3. The sum of O.N. values for all atoms in a compound equals zero. (e.g. Ca(OH)₂) Total O.N here = 0
4. The sum of O.N. values for the atoms in a polyatomic ion equals the ion's charge on the formula unit in magnitude and sign. (e.g. NO₃⁻ = -1)

Rules for specific atoms or periodic table groups

1. For Group IA(1): O.N. = +1 in all compounds (e.g. alkali metals; Na⁺)
2. For Group IIA(2): O.N. = +2 in all compounds (e.g. Mg²⁺)
3. For hydrogen: O.N. = +1 in combination with non-metals
4. For oxygen: O.N. = -1 in peroxides and superoxides)
O.N. = -2 in all other compounds(except with F:
OF₂, O₂F₂, O.N. = -1/2)
5. For Group VIIA(17): O.N. = -1 in combination with metals, nonmetals
(except O), and other halogens (IF₅) lower in the group

Rules for Assigning an Oxidation Number (O.N.)

Rules

6. For Group VIA(16): O.N. = -2
7. For Group VA(15): O.N. = -3 when in their binary compounds with metals

NOTE! Rules 1 to 7 are in descending order i.e. 1 supercedes 2 etc.

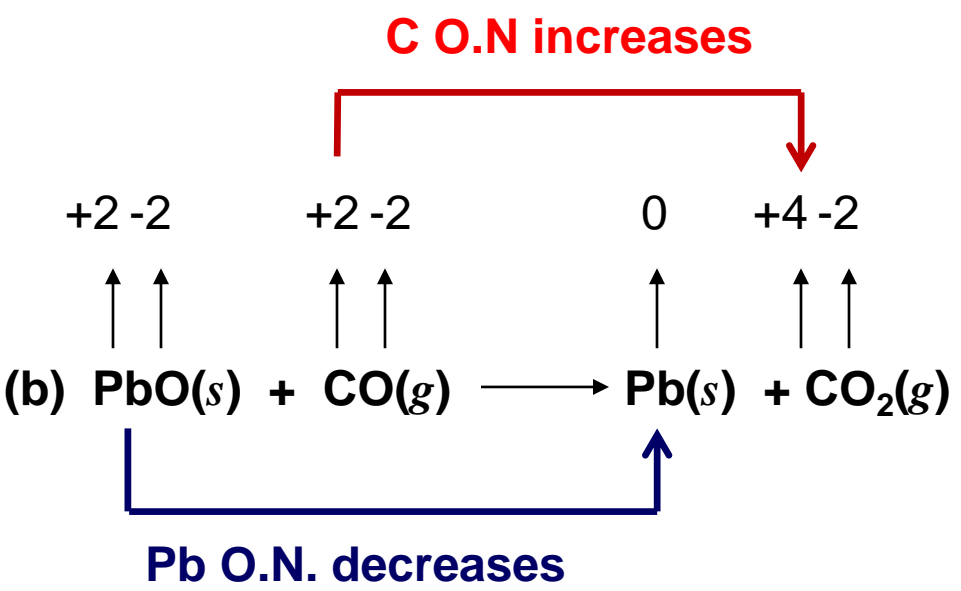
Exercises

- Do exercises from print out to determine oxidation numbers applying the 7 rules given

Sample Problem

Recognizing Oxidizing and Reducing Agents

(Do more from print out)



The O.N. of C increases; it is oxidized; it is the reducing agent.

The O.N. of Pb decreases; it is reduced; it is the oxidizing agent.

WHAT CAN BE SAID ABOUT OXYGEN ATOMS??

Summary: Redox Terminology



OXIDATION

One reactant loses electrons. **Zn loses electrons.**

Reducing agent is oxidized. **Zn is the reducing agent and becomes oxidized.**

Oxidation number increases. **The oxidation number of Zn increases from 0 to +2.**

REDUCTION

Other reactant gains electrons. **Hydrogen ion gains electrons.**

Oxidizing agent is reduced. **Hydrogen ion is the oxidizing agent and becomes reduced.**

Oxidation number decreases. **The oxidation number of H decreases from +1 to 0.**

Balancing Redox Equations

To balance oxidation-reduction reactions in acidic or basic solutions we need to write the chemical equation so that on both sides of equation :

- number of atoms of each element is equal (*mass conserved*)

AND

- sum of +ve and –ve charges is equal (*charge conserved*)

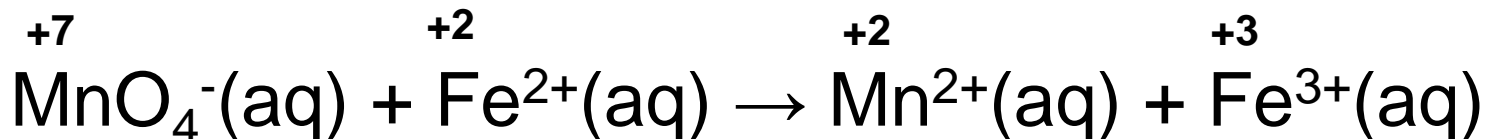
To do this, we'll need to assign oxidation numbers (O.N.) to all atoms.

Balancing Redox Equations

1. Assign oxidation numbers (O.N.) and identify species with O.N. changes
2. Write incomplete half-reactions (oxidation and reduction)
3. Balance each half-reaction separately:
 - a. Balance atoms undergoing redox (put on hold O & H).
 - b. Balance remaining atoms.
 - i. **Add H_2O to balance oxygens.**
 - ii. **Add H^+ to balance hydrogens.**
4. Balance charges by adding electrons to the appropriate side of the equation.
5. Multiply each half-reaction so that the same number of electrons are involved in the reduction and the oxidation.
6. Add the half-reactions, bring same species together and cancel equal amounts of any species occurring on each side of the equation.
7. **In basic solutions, add OH^- (both side) to neutralize H^+ .**

Balancing Redox Equations (Acid Solution)

Consider the following redox reaction:



Note:

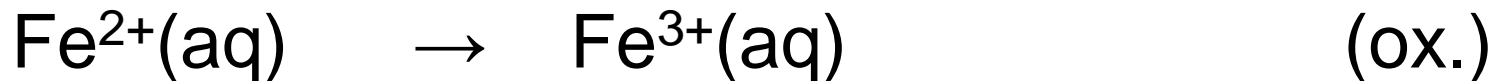
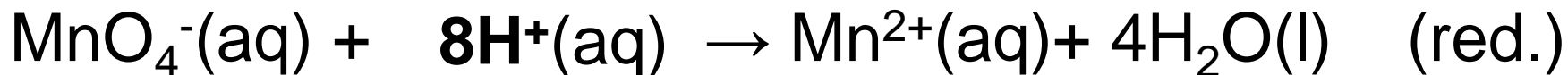
To carry out **step 3**, balance (i) missing oxygen atoms with equal amount of H_2O (ii) missing hydrogen atoms with equal amount of H^+

Balancing Redox Equations (Acid Solution)

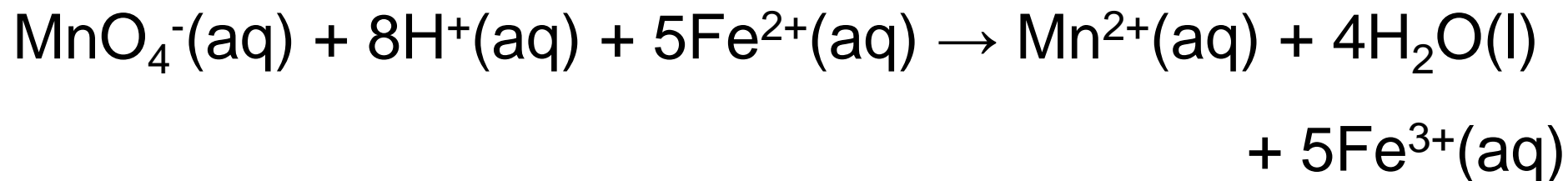
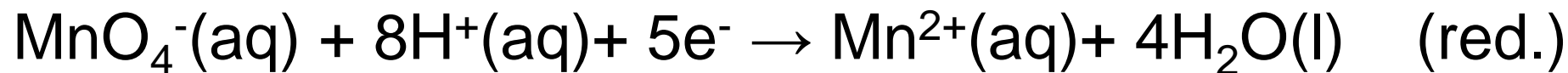
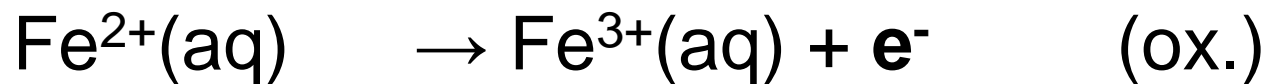
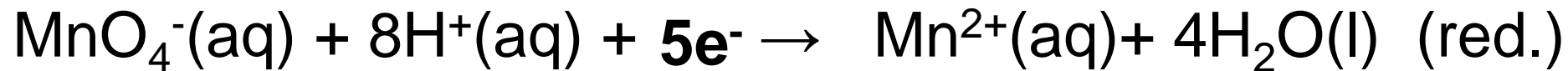
Step 3b (i): Add water to balance the oxygens:



Now H atoms have been introduced, so they need to be balanced with H^+ ions on LHS of equation [i.e. **step 3b (ii)**]:



Balancing Redox Equations (Acid Solution)



Check: Is this equation balanced i.t.o matter and charge

In basic solutions

- **Add OH^- (both side) to neutralize H^+**
- We do examples from print out together

Application: Redox Chemistry

There are many industrial and laboratory applications of redox stoichiometry. For example:

- a mining engineer must know the concentration of iron in a sample of iron ore in order to decide whether or not a mine would be profitable.
- Chemical technicians in industry, monitoring the quality of their companies' products, must determine the concentration of substances such as sodium hypochlorite (NaClO) in bleach, or hydrogen peroxide (H_2O_2) in disinfectants.

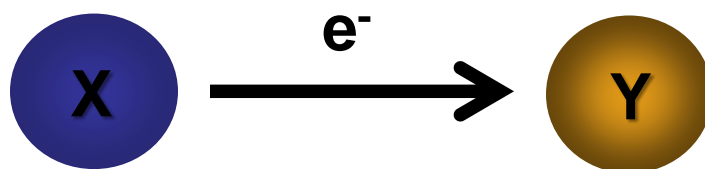
Application: Redox Chemistry

(recall your CHM 191)

- In a titration, one reagent (**the *titrant***) is slowly added to another (**the *sample***) until an abrupt change in a solution property (**the *endpoint***) occurs.
- In acid–base titrations, the titrant is generally a **strong acid or base**.
- In redox titrations, the titrant is always a **strong oxidizing or reducing agent**.

Introduction: Electrochemistry

- **Electrochemistry** is the study of the **transfer of electrons** from one chemical species to another



transfer or shift of electrons

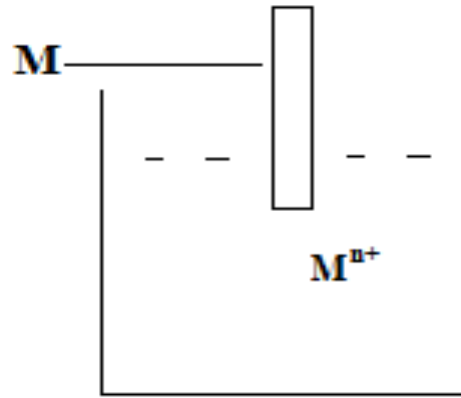
- **In everyday life:**
 - Car battery, *Cell phone battery*
 - Refining of metals; manufacturing of chemicals
- *Why Cutlery or ornaments made of silver tarnish and become black?* $4\text{Ag(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Ag}_2\text{O(s)}$
- Electroplating, galvanizing of metals, etc.

Introduction: Electrochemistry

- **Electrochemistry** can also be put as the study of how chemical reactions can be used to produce electricity¹ and how electricity can be used to produce chemical reactions²
- **i.e. there are two inherently different methods by which an electric current interacts with matter:**

- (1) An electric current can cause a chemical reaction: **Electrolytic Cell**
- (2) A chemical reaction can produce an electric current: **Voltaic/Galvanic cell**

Metal in the solution of its ions



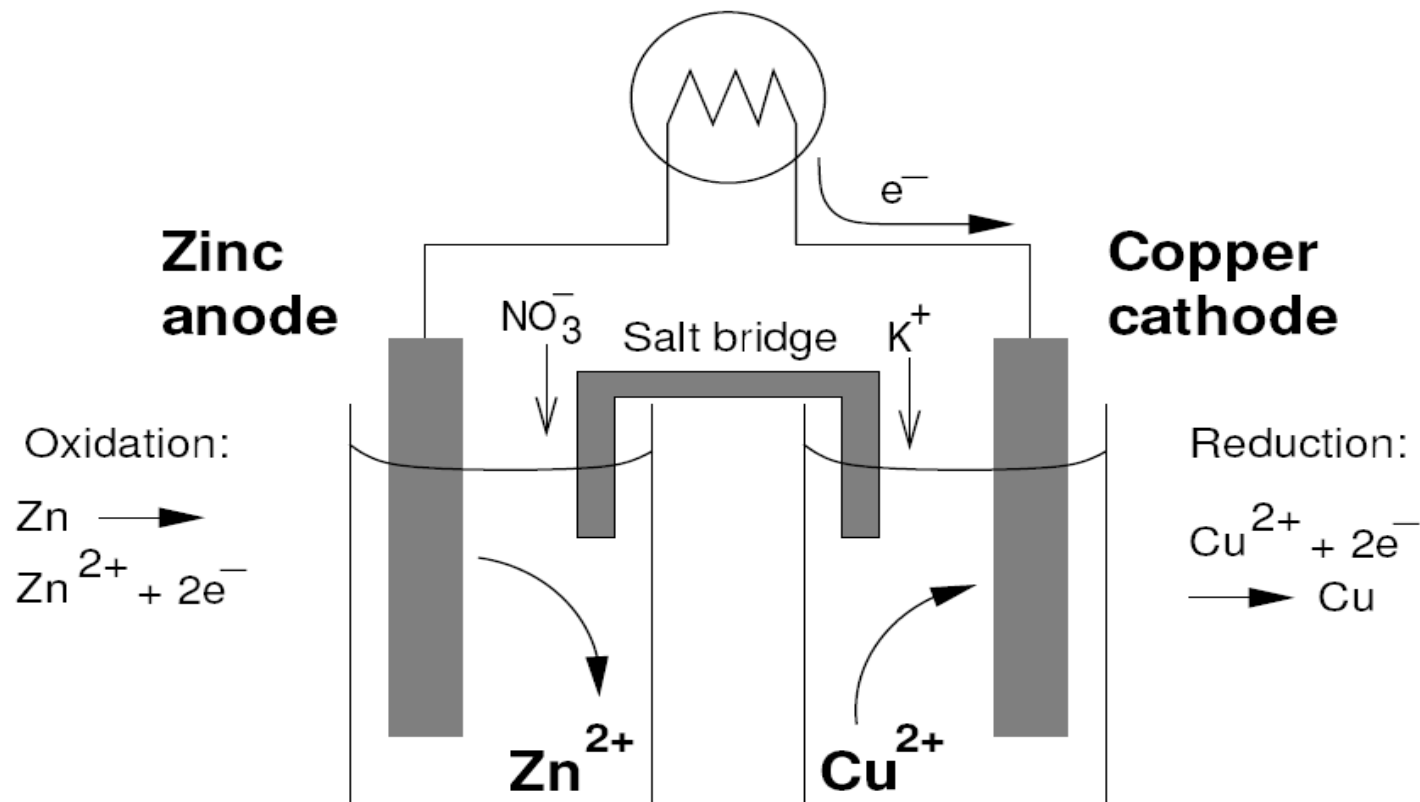
- When a strip of metal, M is put in a solution of its ions M^{n+} then,
- M= electrode-
This is the material, either a metallic rod/bar/strip that allows passage of electrons. There are two types of electrodes (Anode and cathode)

- Anode = It sends electrons into the outer circuit. It has a negative charge and it is shown as (-) in cell diagrams
- Cathode = Electrode at which electrons are received from the outer circuit. It has a positive charge and it is shown as (+) in cell diagrams
- Current- Flow of electrons through a conductor
- Half-cell- Half of an electrochemical cell, it is actually the combination of the metal, M and the solution containing M^{n+} (i.e. electrode and solution). One half is for oxidation while the other half is for reduction.
- The solution is called the electrolyte.

Interaction between Electrode and Electrolyte

- A metal ion M^{n+} may collide with the electrode and undergo no change
- A metal ion M^{n+} may collide with the electrode and gain 'n' electrons and be converted to metal M. The ion is therefore said to be reduced. $M^{n+}(aq) + ne^- \rightarrow M(s)$
- A metal atom may lose 'n' electrons and enter into solution. The metal atom is said to be oxidized.
 $M(s) \rightarrow M^{n+}(aq) + ne^-$
- Overall reaction: $M(s) \leftrightarrow M^{n+}(aq) + ne^-$

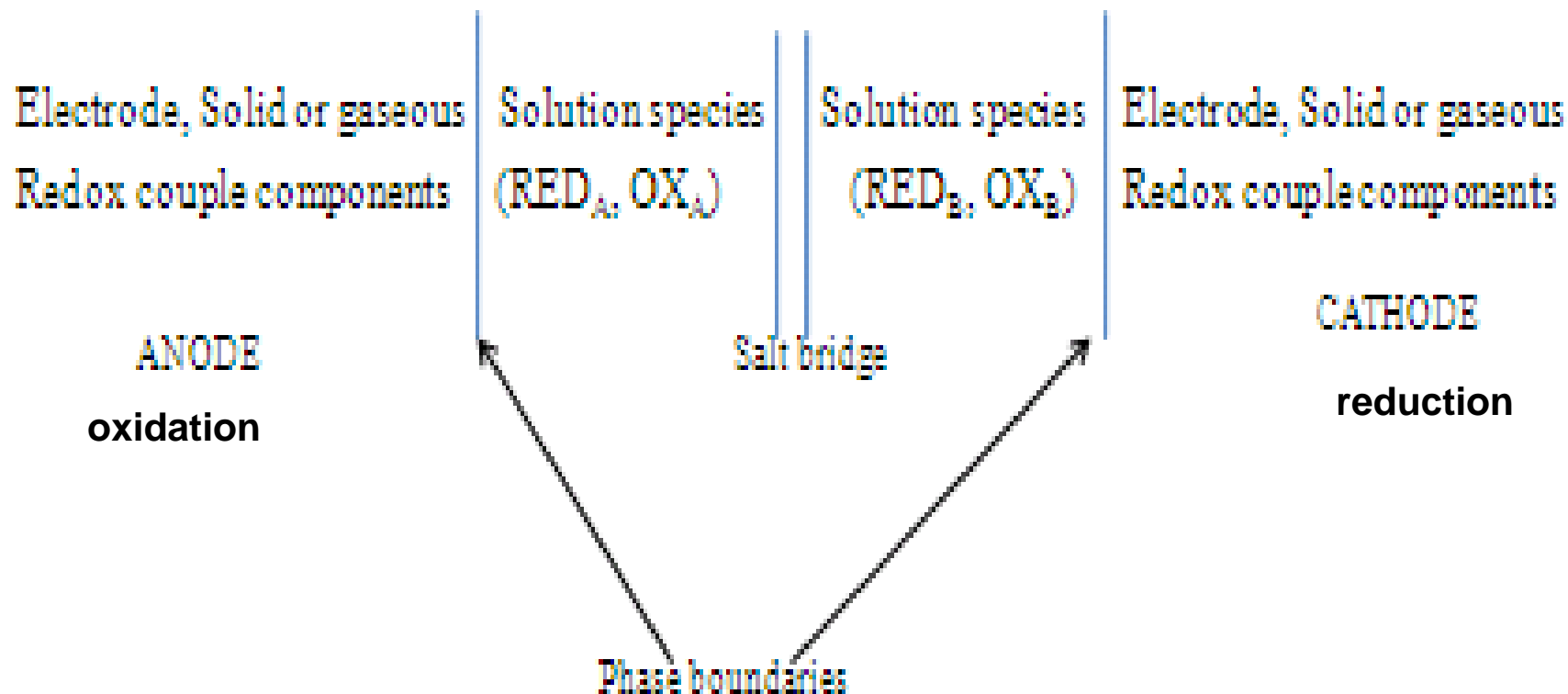
Voltaic Cells



Voltaic Cells: electrochemical cells in which electricity is generated as a result of spontaneous chemical reactions.

Notation: $\text{Zn}/\text{Zn}^{2+} // \text{Cu}^{2+}/\text{Cu}$

Cell Notation



Notation: $\text{Zn}/\text{Zn}^{2+} // \text{Cu}^{2+}/\text{Cu}$

At the anode

- The electrode is made of Zn metal
- The electrolyte is a Zn^{2+} solution (e.g. ZnSO_4)
- Zn metal loses e^- s & is oxidized to $\text{Zn}^{2+}(\text{aq})$
- Electrode is eroded during the process and loses Mass
- Electrons lost by Zn metal passes to the cathode

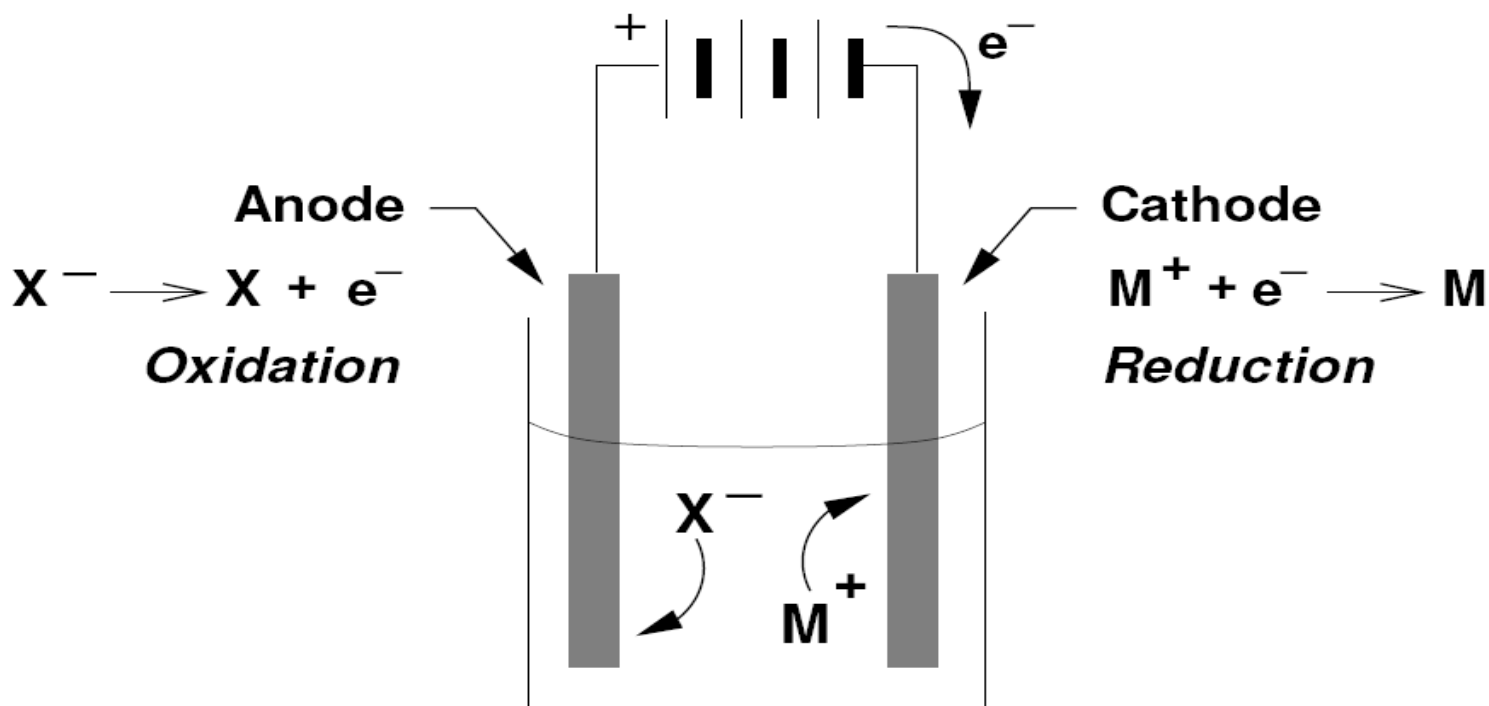
At the cathode

- The electrode is made of Cu metal
- The electrolyte is a Cu^{2+} solution
- Cu^{2+} is reduced to Cu metal
- Copper is deposited on the electrode and it gains mass (since electrons are gained by Cu^{2+} to form Cu)

- **Salt bridge** consists of a tube containing a solution of $\text{KNO}_3(\text{aq})$ and plugged at the ends.
- As Zn is oxidized to Zn^{2+} , excess cations at the anode is neutralized by NO_3^- from the salt bridge.
- As Cu^{2+} is reduced to Cu metal, a negative charge arises at the cathode is neutralized by K^+ from the salt bridge.

Electrolytic Cells

- An electrolytic cell is an electrical arrangement for driving a **non-spontaneous** redox reaction using an **external** electrical energy source



Electrolytic cell

Comparison of Electrochemical cells

- There are 2 main types
- **Voltaic (Galvanic) cells:**
 - ✓ Here, reaction occurs spontaneously
 - ✓ The chemical changes during this reaction produce electricity
 - ✓ They have a positive voltage
 - ✓ Two electrolytes are employed
 - ✓ Assume solutions of equal concentration of 1 M

Comparison of Electrochemical cells

- **Electrolytic cells**

- ✓ Here reactions are non-spontaneous
- ✓ When electricity is applied to this type of cell, a chemical change is produced.

Standard Electrode Potentials

- The relative oxidizing or reducing strengths of redox couples are expressed in terms of their standard electrode potentials (E^θ)
- To measure the E^θ of any redox couples, we arbitrarily choose a reference redox couple in an electrochemical cell.
- The reference redox couple used is $\text{H}^+(\text{aq})/\text{H}_2(\text{g})$, (standard hydrogen electrode (SHE)) which (under agreed standard conditions) is given a E^θ value of zero.

The standard hydrogen electrode (SHE)

- $\text{H}_2(\text{g})$ is passed at 1 atm pressure over an inert Platinum metal surface in a solution of H^+ whose activity is 1 at 25 °C.
- As the $\text{H}_2(\text{g})$ is passed, electrons are released to the H^+ in solution and there is a cycle of reaction (clockwise flow of electrons).
- The SHE is given an E° value (by convention) of 0.00V. All E° values are referenced relative to this zero.

Standard Redox Table

Oxidizing agent	Reducing agent	$E_{\text{red}}^0/\text{V}$
$\text{Li}^+(aq) + e^- \rightarrow$	$\text{Li}(s)$	-3.05
$\text{K}^+(aq) + e^- \rightarrow$	$\text{K}(s)$	-2.93
$\text{Na}^+(aq) + e^- \rightarrow$	$\text{Na}(s)$	-2.71
$\text{Mg}^{2+}(aq) + 2e^- \rightarrow$	$\text{Mg}(s)$	-2.37
$\text{Al}^{3+}(aq) + 3e^- \rightarrow$	$\text{Al}(s)$	-1.66
$\text{Zn}^{2+}(aq) + 2e^- \rightarrow$	$\text{Zn}(s)$	-0.76
$2\text{H}^+(aq) + 2e^- \rightarrow$	$\text{H}_2(g)$	0.00
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow$	$\text{Cu}(s)$	+0.34
$\text{I}_2(s) + 2e^- \rightarrow$	$2\text{I}^-(aq)$	+0.53
$\text{Br}_2(l) + 2e^- \rightarrow$	$2\text{Br}^-(aq)$	+1.07
$\text{Cl}_2(g) + 2e^- \rightarrow$	$2\text{Cl}^-(aq)$	+1.36
$\text{F}_2(g) + 2e^- \rightarrow$	$2\text{F}^-(aq)$	+2.87

This table can be found in any Chemistry 1 textbook

Key Points about E^θ

- The standard states for aqueous ions and gases are 1 M concentration and 1 atm pressure, respectively. The tabulated potentials hold only for standard conditions.
- The half-equations are all written as reductions, and the E^θ apply to the reduction reaction. When the equations are reversed (oxidation), the sign of the E^θ must change.
- It can be applied in many quantitative determination:
 - Determination of strength of an oxidant or reductant
 - **To calculate the standard cell voltage of a cell**
 - **Spontaneity of redox reactions**

Standard Cell Voltage

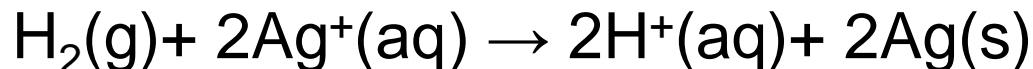
- The standard voltage for a cell-reaction (E^{θ}_{tot}) is the potential difference measured across the cell when all species in solution are at 1 M concentration and all gases are at pressure of 1 atm.
- Procedure to **calc. the standard cell voltage** of a cell
 - Split the cell reaction into half-reactions
 - Look up E^{θ} in a standard table and identify the redn. and oxidation reaction and write against each half reaction
 - E^{θ}_{red} = half cell potential of the reduction reaction
 - E^{θ}_{ox} = half-cell potential of the oxidation reaction

Standard Cell Voltage

- Change the reduction equation of the half-cell reaction with lower value of E^θ to an oxidation equation. The sign of the E^θ value will also change
- Balance the number of electrons in the two half equations (**NOTE, this does not affect the E^θ since it is an intensive property**)
- Add up the two half equations and do the same to the E^θ
- $E^\theta_{\text{tot}} = E^\theta_{\text{red}} + E^\theta_{\text{ox}}$, where E^θ_{tot} (or E^θ_{cell}) is the standard cell voltage

Standard Cell Voltage: Example

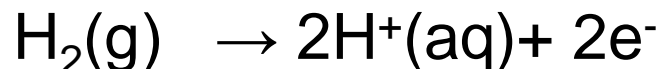
Q. Given the cell reaction, calculate the standard cell potential of the cell:



A. Half reactions:

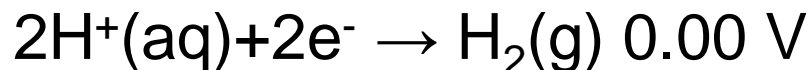
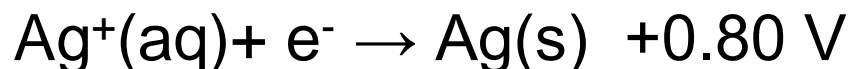


reduction

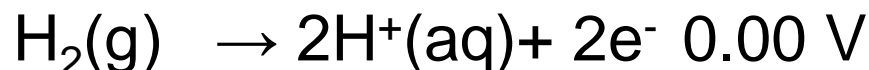


oxidation

From the table:



Reverse the hydrogen half-reaction: (**Note sign changes where applicable**)



$$\text{Now: } E^\theta_{\text{tot}} = E^\theta_{\text{red}} + E^\theta_{\text{ox}} = (0.80 + 0.00) \text{ V} = +0.80 \text{ V}$$

NOTE

- The values of E^θ are independent of the number of electrons transferred, therefore,
- **DO NOT MULTIPLY BY
STOICHIOMETRIC COEFFICIENTS!**

Spontaneity of Redox Reactions

Remember: Gibbs Free Energy Change in a cell; $\Delta G = \Delta H - T\Delta S$

ΔG = Gibbs' energy change

ΔH = enthalpy change

T = temperature and

ΔS = entropy change

Note: Maximum useful workdone by a system at constant pressure = ΔG

Workdone by a system is negative

For electrochem., $W_{\max} = W_{\text{elec.}}$

$$\therefore \Delta G^\theta = -W_{\max} = -nFE^\theta_{\text{tot}}$$

W_{\max} = maximum amount of work reactant can produce

n = number of moles of electrons

F = Faraday's constant (96485 C.mol⁻¹)

Spontaneity of Redox Reactions

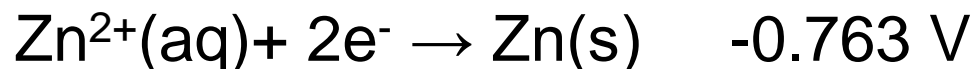
$$\Delta G^\theta = -w_{\max} = -nFE^\theta_{\text{tot}}$$

Deductions:

- A positive E^θ_{tot} means a negative ΔG^θ and a spontaneous forward reaction
- A negative E^θ_{tot} means a positive ΔG^θ and a non-spontaneous forward reaction
- A zero E^θ_{tot} means the cell is in equilibrium and there is no net reaction in either direction

Example

Work out ΔG^0 for the following reaction:



Remember:

$$\Delta G^0 = -nFE_{\text{tot}}^0$$

The oxidation state of the Zn changes from 0 to +2, so two electrons were transferred.

$$\begin{aligned} \Delta G^0 &= -2 \times 96485 \text{ C mol}^{-1} \times 2.121 \text{ J C}^{-1} \\ &= -409.3 \text{ kJ mol}^{-1} \end{aligned}$$

Note : $1 \text{ V} = 1 \text{ J C}^{-1}$
More examples from your print out

Standard cell potential and Equilibrium constant K_{eq}

Recall from Thermodynamics: $\Delta G^0 = -RT \ln K_{eq}$

Also, that $\Delta G^0 = -nFE_{tot}^0$

Re-arrange to get: $E_{cell}^0 = \frac{RT}{nF} \ln K_{eq}$

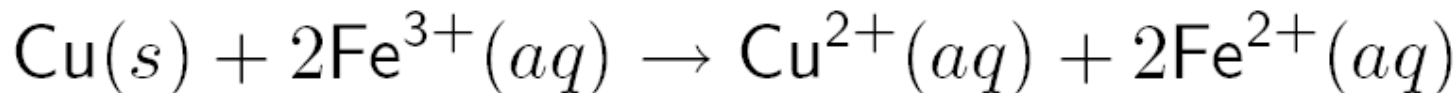
$$E^0 = \frac{2.303RT}{nF} \log K$$

At standard conditions, $T = 25^\circ\text{C}/298\text{K}$, $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$, $F = 96485 \text{ C/mol of e}^-$

$$E_{cell}^0 = \frac{0.0592}{n} \log K$$

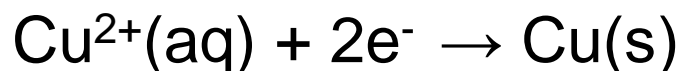
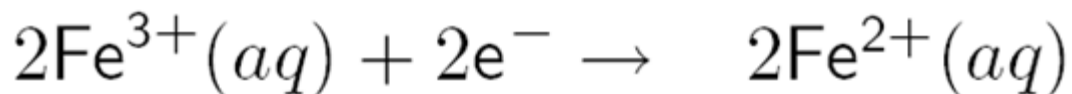
Example

Q. Given that :



the cell potential is 0.431 V, calculate K_{eq} at 298 K.

A. Balanced half equations to know no. of electrons



$$E_{\text{cell}}^0 = \frac{RT}{nF} \ln K_{\text{eq}}$$

$$\therefore \ln K_{\text{eq}} = E_{\text{cell}}^0 \times \frac{nF}{RT}$$

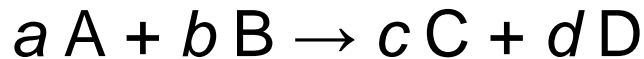
$$= 0.431 \text{ J C}^{-1} \times \frac{2 \times 96485 \text{ C mol}^{-1}}{8.31 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}$$

$$= 33.6 \text{ (dimensionless)}$$

$$K_{\text{eq}} = e^{33.6} = 4 \times 10^{14} \text{ (dimensionless)}$$

The Nernst Equation

- The Nernst equation shows relationship between E^0 and concentration of reactants. Consider a reaction:



$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

From Thermodynamics, $\Delta G = \Delta G^0 + RT \ln K$

OR, $\Delta G = \Delta G^0 + 2.303 RT \log K$

$$\Delta G = -nFE_{\text{cell}}; \Delta G^0 = -nFE^0_{\text{cell}}$$

$$-nFE_{\text{cell}} = -nFE^0_{\text{cell}} + RT \ln K$$

Divide through by $(-nF)$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT \ln K}{nF} \text{ or } E_{\text{cell}} = E^0_{\text{cell}} - \frac{2.303 RT \log K}{nF}$$

The Nernst Equation

- Inserting K:

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ or } E_{cell}^0 - \frac{RT}{nF} \ln \frac{\text{oxidized}}{\text{reduced}} \text{ or } E_{cell}^0 - \frac{RT}{nF} \ln M^{n+}$$

- $$E_{tot} = E_{tot}^{\theta} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

E_{tot} = potential under non-standard conditions

E_{tot}^{θ} = potential under standard conditions

$RT/F = 0.0592$

n = the number of moles of electrons, and

$[]$ = concentrations

Example (check print out for more)

Q. Calculate the value of E for the oxidation of iron(II) to iron(III) in a solution of 0.100 M Fe^{2+} and 0.500 M Fe^{3+} according to the following equations:



A.

$$E_{\text{tot}} = E^{\theta}_{\text{tot}} - \frac{0.0592}{n} \log \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

$$E_{\text{tot}} = E^{\theta}_{\text{tot}} - \frac{0.0592}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

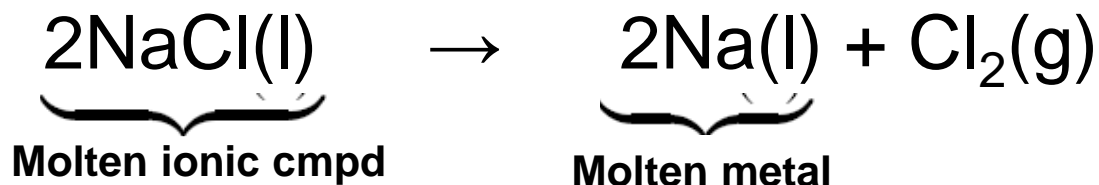
$$= -0.771 - 0.0592 \log \frac{(0.500)}{(0.100)}$$

$$= -0.771 - 0.0414$$

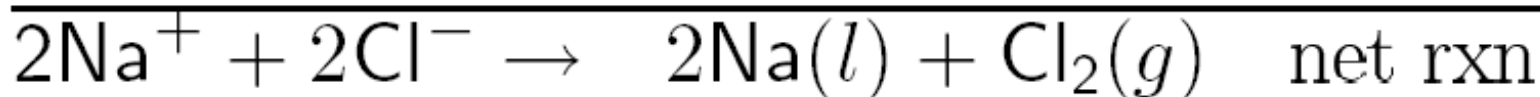
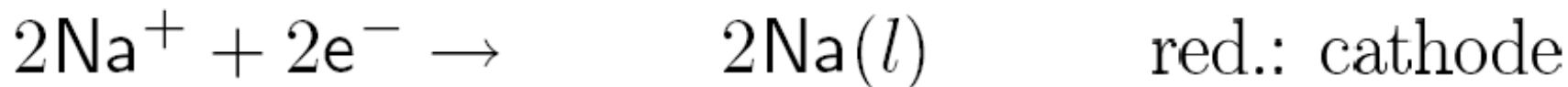
$$= -0.812 \text{ V}$$

Example of Electrolysis: Ionic Compound

In the reaction:



Two half-reactions:



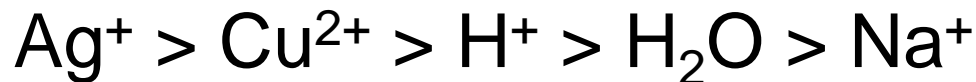
Electrolysis in Aqueous Solution

At the cathode, possible reactions are:

- $M^{n+}(aq) + ne^{-} \rightarrow M(s)$ for M = Transition metal
- $2H^{+}(aq) + 2e^{-} \rightarrow H_2(g)$ in solution of strong acid (HCl)
- $2H_2O + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$ (If cation in solution is group 1 or 2 metal or aluminium)

Generally:

The ease of *reduction* is



Electrolysis in Aqueous Solution

At the anode, possible reactions are:

- $X^{n-}(aq) \rightarrow X + ne^-$ if $X = \text{Halogen}$)
- $2OH^-(aq) \rightarrow 1/2O_2(g) + H_2O(l) + 2e^-$ (in solution of strong base, e.g. = NaOH)
- $H_2O \rightarrow 1/2O_2(g) + 2H^+(aq) + 2e^-$ for anions which are difficult to oxidize, e.g. F^- , NO_3^- , SO_4^{2-}

Generally:

The ease of *oxidation* at the anode is:



Application of Electrolysis

- Extraction of metals like: sodium, magnesium, aluminium, etc.
- Industrial-scale manufacturing of chemicals (e.g., chlorine)
- Electroplating, galvanization of metals etc.