# 16 – Redox equilibria

## Redox review

Oxidation - e- #o - agents are Reduced to Oxidize other molecules

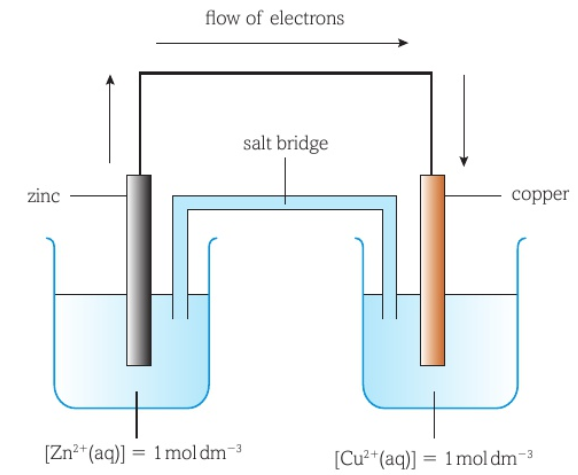
Reduction - e- #o - agents are Oxidized to Reduce other molecules

Disproportionation reaction - Elements of the same compound undergoes both oxidation and reduction

Standard conditions - 100kPa, 298K, 1 mol dm-3

## Electrical chemical cell

Standard electrode potential - Potentials measured of cell against std. H2 electrode at standard conditions



Largerreduced, smaller oxidized

Largerstronger oxidizing / weaker reducing agents

Flipping ECS formulas flips the sign of

(Zn oxidized, Cu reduced)

Electrolytes (aq in beaker) must be **soluble**. (Nitrates used as always soluble)

Salt bridge: NaCl

### Electro-cell diagram

e- flows from smaller larger

Left oxidized, right reduced.

### Shorthand display

Example:

### Measuring

The standard hydrogen electrode is used to measure.

Swap out H2 with anything if different potential is measured.

Half equation:

A reference electrode (H2) is needed as we can only measure a potential difference

Porous Pt is used as to increase surface area

### Feasibility

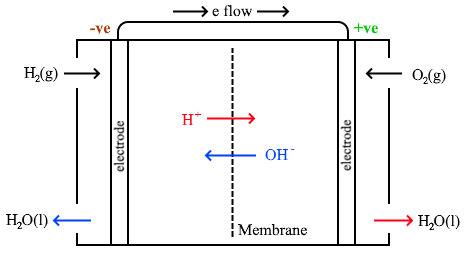
Kinetically stable -

Thermodynamically stable -

reaction is feasible (spontaneous).

This only predicts that reaction is possible, not that it will occur as it depends on factors like

## Hydrogen-Oxygen Fuel cells

* Both sides overall equations are the same: (so same )
* The membrane separates H2 and O2 gases
* Electrodes are coated in Pt as catalyst
* Alkali / Acid is used as electrolytes allowing movement of H+

### Electrolyte equations

Anode:

Cathode:

Acidic: add H+

Alkaline: add OH-

**Acidic**

Anode (-):

Cathode (+):

**Alkaline**

Anode (-):

Cathode (+):

### Advantages & disadvantages

|  |  |
| --- | --- |
| * Environmentally friendly * No harmful product pollutants * Alternative to use of fossil fuels | * H2(g) is a flammable gas * H2(g) is not renewable * Storage of H2(g) has hazards * Storage of H2(g) is costly |

## Titration related

Common color change:

Color change: PurplePale pink

Acidic conditions are used to prevent formation of (brown p.p.)

# 17 – Transitional metals

Transitional metals - Metals that can form > 0 stable ions with partially filled d subshell

## Electronic configuration

If moving 4s e- to 3d, d is d5 / d10, there is more stability for half-filled subshells, so e- would leave 4s.

When forming ions, 4s e- leaves first.

[Ar] corresponds to configuration up to 3d6

## Introduction to complexes

Ligands - Species with lone pair of e- that can form dative bond to t.m. ion

Co-ordinate bonds (c.o. bonds) - Dative covalent bond from ligands

Co-ordination number (c.o. num) - Number of c.o. bonds



### Shapes

Large ligands (Cl-) 4 bonds: Tetrahedral 109.5°

Small ligands (H2O / NH3) forms 6 bonds: Octahedral 90°

*Number of ligands around metal:*

* Ligands repel each other as far as possible
* Giving shape with bond angles of X°

### Naming

H2O aqua | NH3 ammine | X- halo | OH- hydroxo (All negatives end with -o)

### Multidentate ligands

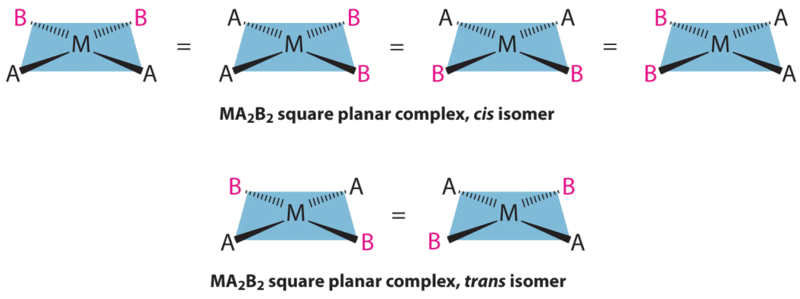
Multidentate ligands - Ligands that has > 1 lone pair of e- that can bond to t.m. ion

Names of multidentate is related to number of c.o. bonds formed.

### Ligand isomerism

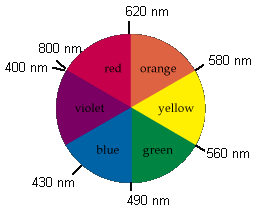
Optical isomerism: only 3 bidentate ligands

Cis-trans geometric isomerism: quad-bi octahedral ligands / bi-bi square planar ligands

Cis - same side | Trans - opposite side

## Complex reactions & color

### Cause of colors – 3d Energy levels

1. Partially filled d-orbital
2. Ligands cause d-d splitting
3. Visible spectrum radiation absorbed
4. Light causes d-d transitions
5. Complementary color observed

If no partially filled d-orbital, there will be no d-d transitions hence no color

### Reactions

1. Deprotonation Ligands ± H+
2. Ligand exchange Ligands replaced
3. Redox Oxidation number
4. C.o. number change Number of ligands in complex

## Summary of reactions

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Type** | **Ligand** | **Formula** | **Exception** | **Metals** |
| D | OH- |  |  | All |
| D | OH- (Excess) |  |  | **Cr Zn** |
| D | NH3 |  |  | All |
| L | NH3 (Excess) |  |  | **Cu Co Cr Ni Zn** |
| L | Conc. Cl- |  |  | **Cu Co** |

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **T.M.** | **Oxi.** | **Color** | | | **OH- / NH3** *p.p.* | | **Excess OH-** *sol.* | **Excess NH3***sol.* | **Conc. Cl-** |
| Cu | 2 | B | | | B | |  | B | dBr |
| Co | 2 | P | | | B | | Br | B |
| Cr | 2, 3, 6 | B | G | Y | G | | G | G |  |
| Ni | 2 | G | | | G | |  | B |
| Zn | 2 | c | | | W | | c | c |
| Fe | 2, 3 | pG | Y | | dG | Br |  |  |
| Mn | 2 | pP | | | W | |

* Fe2+ turns to Fe3+ upon standing (Dark green to brown)
* Most other reactions can be explained by ECS balancing & comparison

### Chromate reactions

Use ECS to form equations.

## Catalyst properties

Transitional metals can form compounds with catalytic properties.

### Homogeneous

* Phase: Same phase as [R]
* Mechanism: React with [R] to form **intermediates → products** + **re-form** catalyst
* Reformation: Yes

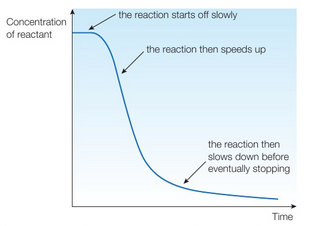
Note that the Ea of forming intermediate + products is lower than the uncatalysted reaction

### Heterogeneous

* Phase: Different phase as [R]
* Mechanism:

1. R A**d**sorb onto surface
2. Weakens bond in R
3. Products then desorb

∴Surface area ↑Rate ↑

**Support mediums** are used to ↑area → ↓cost

* Reformation: Not used up

Advantage over homo: Does **not need separation from products**

### Autocatalysis

**Product of reaction acts as catalyst**: [P] ↑→ rate ↑

* Phase: Same phase as [R]
* Mechanism:

1. Reaction is slow at start
2. Catalyst [P] is formed → reaction speeds up (rate↑)
3. [R] ↓→ reactions slows down (rate↓)

* Reformation: None after reaction

# References

## Solubility rules

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Soluble** | | | | | **Exceptions** |
| Nitrate | Ammonium | Potassium | Sodium |  | - |
| Chlorine | Iodine |  |  |  | Pb2+ Hg22+ Ag+ (PHAg) |
| Sulphate |  |  |  |  | Pb2+ Hg22+ Ag+ Ca2+ Ba2+ Sr2+ (Castro bear) |
| **Insoluble** | | | | |  |
| Carbonate | Phosphate |  |  |  | Group 1, NH4+ |
| Hydroxide |  |  |  |  | Group 1, NH4+ Ca2+ Ba2+ Sr2+ (Castro bear) |