# 16 – Redox equilibria

## Redox review

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

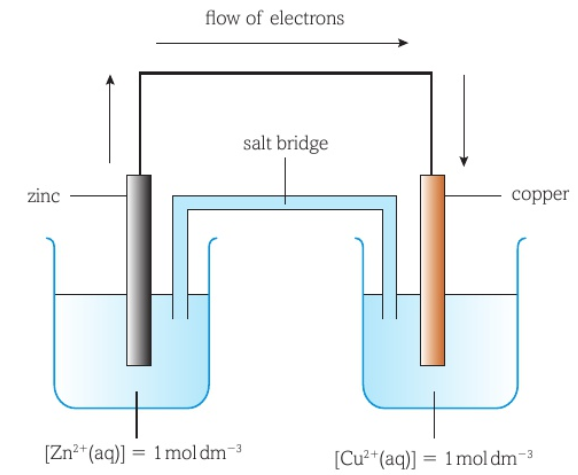
Reduction - e- #o - agents are Oxidized to Reduce other molecules

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
* If both elements are aqueous, use Pt electrode and solution containing both
* Finding conc. of original sol. in equal volume mixed solution must take   
  mol of elements in solution into account:  
  e.g. &

(Zn oxidized, Cu reduced)

Electrolytes (aq in beaker) must be **soluble**. (Group 1 nitrates used as always soluble)

Salt bridge: NaCl

### Electro-cell diagram

e- flows from smaller larger

Left oxidized, right reduced.

### Shorthand display

**Example 1:**

**Example 2:**

* Pt used as both aqueous
* Solution fields must show oxidation (left) and reduction (right)

### 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

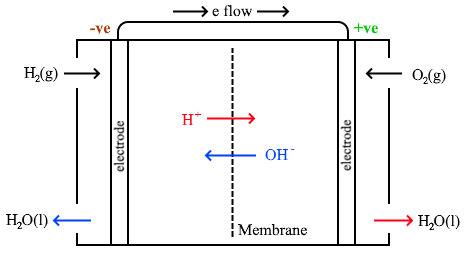
Kinetically stable -

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: PurpleColorlessPale 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°

Ions with more shells can contain more ligands as they have more space for bonding

*Explain shape of compound*

* Ligands repel each other as far as possible
* n lone pairs are donated to the metal ion
* Giving shape with bond angles of X°

### Naming

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

### Multidentate ligands

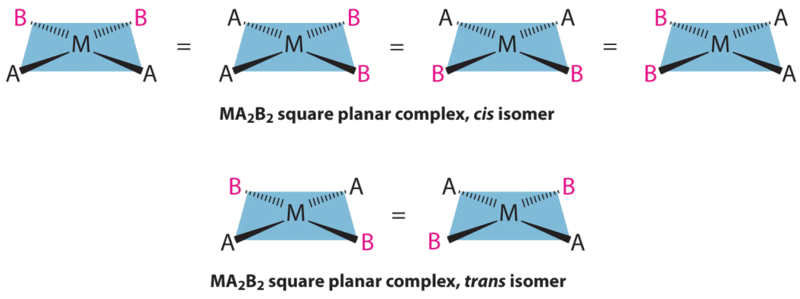
Multidentate ligands - Ligands that has > 1 lone pair of e- that can bond to t.m. ion

EDTA4- is a hexadentate (6) ligand

### Ligand isomerism

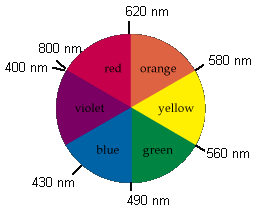
Optical isomerism: only 3 bidentate ligands

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

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

#### Colorless compounds

1. No partially filled d-orbitals
2. No d-d transitions

## Summary of reactions

1. Deprotonation Ligands ± H+
2. Ligand exchange Ligands replaced

|  |  |  |  |
| --- | --- | --- | --- |
| **Type** | **Ligand** | **Formula** | **Exception** |
| D | OH- |  |  |
| D | OH- (Excess) |  |  |
| D | NH3 |  |  |
| L | NH3 (Excess) |  |  |
| L | Conc. Cl- |  |  |

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **T.M.** | **Oxi.** | **Color** | | | **[D] OH- / NH3** *p.p.* | | **[D] Excess OH-** *sol.* | **[L] Excess NH3***sol.* | **[L] 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)
* upon vigorous shaking due to oxidation by O2
* Most other reactions can be explained by ECS balancing & comparison

### Chromate reactions

Use ECS to form equations.

### Vanadium colors

Reversed pattern.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
| +2 | +3 | +4 | +5 |

## Catalysts

* Works by providing alternative pathway with lower Ea
* T.M. compounds are effective catalysts because they can have multiple oxidation states

### Heterogeneous

* Different phase as reactant
* Mechanism:

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

#### Contact process

#### Haber process

Pt oxidized by O2

### Homogenous

* Same phase as reactant
* Mechanism:
  + Uncat. Rx involves same charged ions reacting
  + Cat. Rx involves oppositely charged ions reacting

# 18 – Funny looking ring

“Compare and contrast” requires you to state **similarities** and **differences**!

## Disproving Kekule structure of Arene

|  |  |
| --- | --- |
| Phenomenon | Explanation |
| of reaction with H2 is less than expected | Delocalization of 149 kJ mol-1 more stable than Kekule |
| All C-C bond in Arene has the same length | Delocalization of same bond length instead of diff for C=C |
| Br water is not decolorized | Delocalization of more stable Substitution instead of addition occursstability maintained |

## Arene reactions

Reaction with oxygen:

Halogenation: (ArBr3 cat.)

Friedel-crafts alkylation: (AlCl3 cat.)

Friedel-crafts acylation: (AlCl3 cat.)

Sulfonation: (Ar warmed with sulfuric acid)

Nitration: (H2SO4 & HNO3 reactant, <30°)

* Low temperature prevents further substitutions

### Explaining reaction speeds

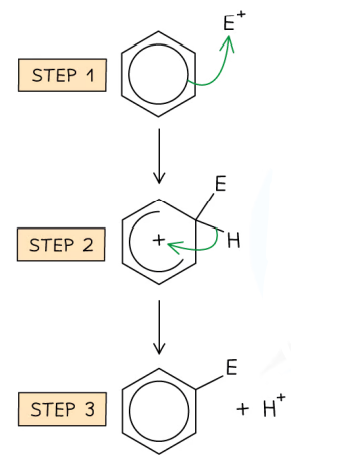
**Alkylarene:** alkyl group donates e- to ring, making it a stronger nucleophile

**Phenol**:

1. OH group attached to ring
2. lone pair of e- on O overlaps with cloud & donated to the ring
3. e- density of ring increased

### Mechanism – Electrophilic substitution

Step 0 – Prepare E+: or



1. C has partial +ve charge
2. E+ has lone pair e- which moves to C
3. Bond to leftover E part breaks

Ring opening facing C-H

Arene ring is e- rich

### Preparing aromatic amines [R]

(Tin [Sn] mixed with HCl, heat under reflux)

### Phenol reactions

Arene ring is e- rich

Bromination: (Room temp.) (Orange sol.white p.p.)

## Arene stuff

* To find isomers of molecular formula,  
  compare distances relative to one group on arene ring
* To find chemical environments, use distance from alkyl group

# 19 – Nitrogen Organic Chemistry

## Amines RNH2

### Preparation

Halogenoalkanes: (Excess, hot ethanolic NH3 under pressure) [NS]

Nitriles reduction: (LiAlH4)

Nitriles catalyzed: (Nickel catalyst)

### Basicity

Higher availability of N lone pair e-stronger base

2° > 1° > NH3 > ArNH2

∵ Alkyl groups are e- pushing

∵ Lone pair is pulled into arene ring

* Amines acts as base as

### Reactions

*Amine / phenylamine have the same reactions*

With acids: (revert with OH-)

With acyl chlorides:

Halogenation:

2° to 3°:

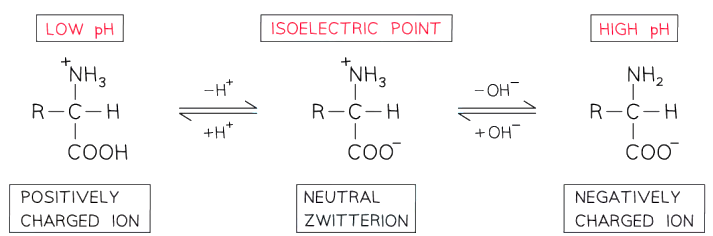
3° to 4°:

## Amino acids

Compounds that contain NH2 and COOH functional groups

* They are amphoteric, acting as both acid and base. The “R” group decides the basicity
* Amino acids undergoes reaction of amines with acids & carboxylic acid with bases
* Identify different amino acids with Chromatography
* **CONH** group formed by polymers of amino acids is called a peptide bond

Solid or aqueous amino acids exists in the form of **zwitterions** (Neutral as solid)

* Charges promote strong intermolecular forces of attraction intermolecularly
* All amino acids are neutral in solution
* Solution in water acts as buffer solutions

## Condensation polymerization

## Azo compounds

Azo / diazonium compounds are organic compounds with the group

### Preparation

1. Formation of nitrous acid: (5° NaNO2 + dilute HCl)
2. Formation of diazonium ion: (5°)

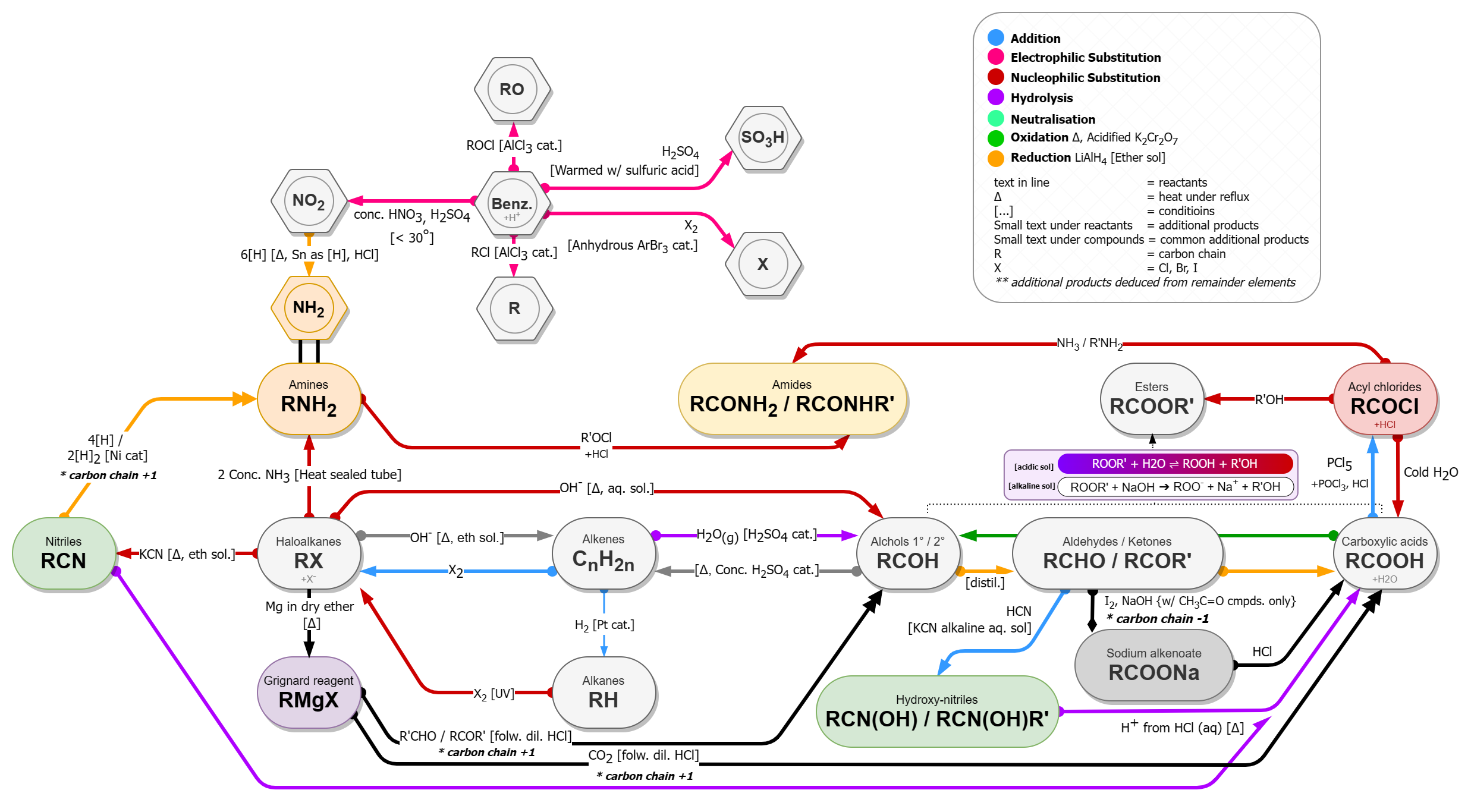
* **>5°** Phenol forms
* **<5°** Reaction too slow

1. Coupling reaction: (Alkaline sol., OH group opposite to N)

# 20 – Organic synthesis & analysis

Even if you’re told to prepare **A** from **B**, you can use something else as a base before using **B**

Most commonly, that’d be using **Haloalkanes** to make a Grignard reagent first before combining with **B**



## Naming

|  |  |  |
| --- | --- | --- |
| Alcohol  Aldehydes  Carboxylic acid  Ketone  Esters  Nitriles  Amines  Amides | R-OH  R-CHO  R-COOH  R-CO-R’  R-COO-R’  R-C≡N  R-NH2  R-ONH-R’ | -ol  -al  -oic acid  -one  R’-yl R-oate  -nitrile  -amine  N-R’-yl R-amide |

## Combustion analysis

## Methods of separation

Distilling Get (l) w/ b.p. << others

Steam distilling Get insoluble (l) from (aq)

Extracting Get wanted organic product

Washing Remove impurities from (s) / (l)

Drying Remove H2O

Filtration Remove (s) from (l)

## Extending carbon chains

### Grignard reactions

Preparing Grignard reagent: (dry ether, heat under reflux)

* Carbon atom attached to Mg is **negative and nucleophilic**

Reactions (followed by reaction with):

1. Acids
2. 1°
3. 2°
4. 3°

## Shortening carbon chains

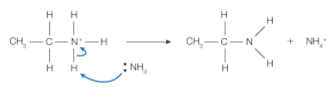
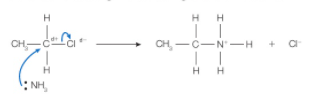
(Warm alkaline aq. I2)

## Calculating final oxidation state

1. Identify the 2 reactants, and one of the half-equations
2. Find the mol ratio R:R
3. The mol ratio is proportional to the e- ratio between the two half-equations

# Essentials

## Nucleophilic substitution



Arrows in mechanism diagrams represent movement of (lone) **electron pairs**:

From bond: Bond breaks (One bond breaks in the case of double bonds)

From atom: Bond forms

## Bonding and structure

Number of p ↑ Outer shell to nucleus attraction ↑ Ionic radius ↓

Unpaired electrons in atoms = e- that are in whole orbitals that aren’t full

## NMR Spectroscopy

### Answering NMR questions

State the following:

1. n of ChemEnv

2. n of Split

3. Reason for split

4. Ratio of areas

5. Position of peaks

* Position of peaks are the chemical shifts of corresponding atoms
* n of peaks n of X in diff ChemEnv
* Ratio of (area of) peaks Ratio of amounts of ChemEnv

### Chemical environments

For atom X: Z1-X-Z2 *Z includes its adjacent atoms*

If Z1 and Z2 is not the same for atoms of X, they are in a different chemical environment.

🡪 Different chemical environments **do** **not** imply different chemical shift ranges!

### 1H High resolution split peaks

For specific H0 atom: H0-C-CHN Splitting of H0’s peak: (N+1)

For -NH2 & -OH, these protons **do not** **count** as adj. protons and **has** **no** adj. protons.

*To explain why there are splits, state how many adjacent protons are there.*

## The Equilibrium constant

For reaction wA(s) + H2O + xB(g) ⇌ yC(g) + zD(g)

|  |  |
| --- | --- |
|  | * Conc. of H2O is always 1 so omit in equation * If reaction is homogenous (R & P same phase) then all solutions include in Kc |
|  | |

## Factors affecting the equilibrium constant

**Only Temperature** affects K. Temperature shifts equilibrium, and hence changes the ratio of K.

Pressure and concentration **do not** affect K as at equilibrium the effect balances out, since the partial pressure of all things changed.

## Titration color change

At the end point, there will be no more reactant and hence only titrate left in solution, so the color at the end point is the color of the indicator in the presence of titrate / solution left.