

A2 Chemistry
Revision Notes / Lightweight Textbook
Volume 1. Organic Chemistry

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Chapter 25 Benzene (and its derivatives)

25.1 Naming

Compounds containing the benzene ring are called aryl or aromatic compounds.

Organic hydrocarbons containing one or more benzene rings are called arenes.

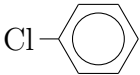
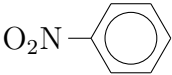
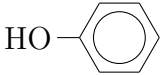
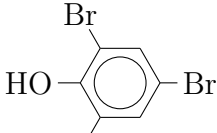
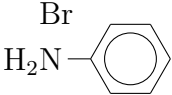
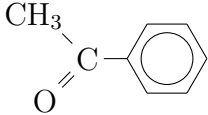
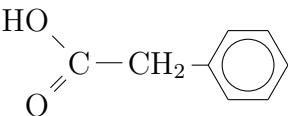
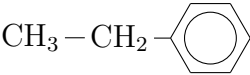
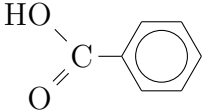
Skeletal Formula	Name
	Chlorobenzene
	Nitrobenzene
	Phenol
	2,4,6-tribromophenol
	Phenylamine
	Phenylethanone
	Phenylethanoic acid
	Ethylbenzene
	Benzoic acid

Table 25.1: Some common aromatic compounds and their names

25.2 Benzene Intro

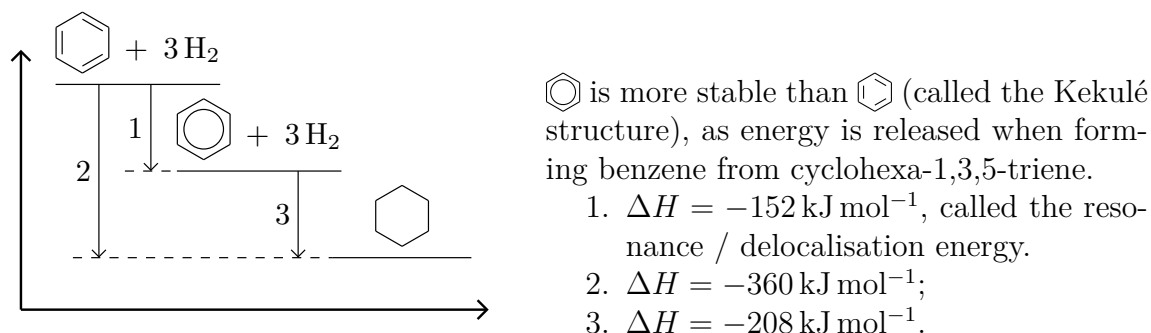


Figure 25.1: Enthalpy changes of hydrogenation of the Kekulé structure and modern benzene structure to cyclohexane

π -bonds in benzene spread over all six carbon atoms and forms a delocalised system.

The big π -bond in benzene is formed due to the overlap of p-orbital electrons from all six carbons.

Benzene has a planar ring structure where all six carbon atoms are equivalent. The evidence for why benzene has a special structure is listed below:

- It does not decolourise bromine water;
- It has a perfect hexagonal shape where all bond lengths are the same. It is symmetric.
- Only three isomers of dibromobenzene can be formed.
- Enthalpy changes of hydrogenation (See Figure 25.1)

25.3 Reaction of arenes

The benzene ring is an stable electron-rich environment, so a strong electrophile is needed to break the π -bonding system.

25.3.1 Electrophilic Substitution

Mechanism:

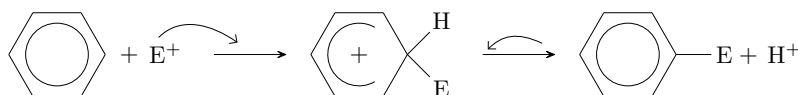


Figure 25.2: Benzene electrophilic substitution with electrophile E^+

Catalyst used for substitution with Br_2 or Cl_2 : FeX_3 or AlX_3 .¹

¹I prefer to use FeBr_3 and AlCl_3 .



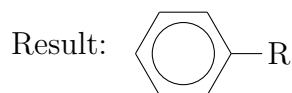
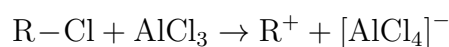
Figure 25.3: Mechanism to generate the electrophile

Nitration of benzene uses concentrated HNO_3 and concentrated H_2SO_4 at 55°C to generate the electrophile NO_2^+ . (The charge is on the nitrogen atom.)

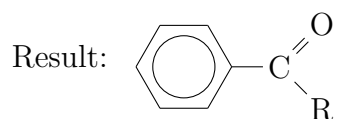
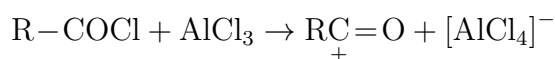


Alkylation and acylation of benzene is done using the Friedel-Crafts process.

- Alkylation: Uses $\text{R}-\text{Cl}$ and AlCl_3 catalyst.




- Acylation: Uses $\text{R}-\text{COCl}$ and AlCl_3 catalyst.



25.3.2 Oxidation of side chains

For almost all cases, adding acidified/alkaline KMnO_4 to a aromatic compound with an alkyl side chain and heating under reflux results in benzoic acid / benzoate. Note:

- If the target compound is benzoic acid, you need to either use acidified KMnO_4 , or use alkaline KMnO_4 AND THEN refluxing it with a dilute acid (preferably H_2SO_4).
- This only works if the branch has a hydrogen on the first carbon atom. 1,1-dimethylethylbenzene , for example, cannot be oxidised using only KMnO_4 .

25.3.3 Diazotisation

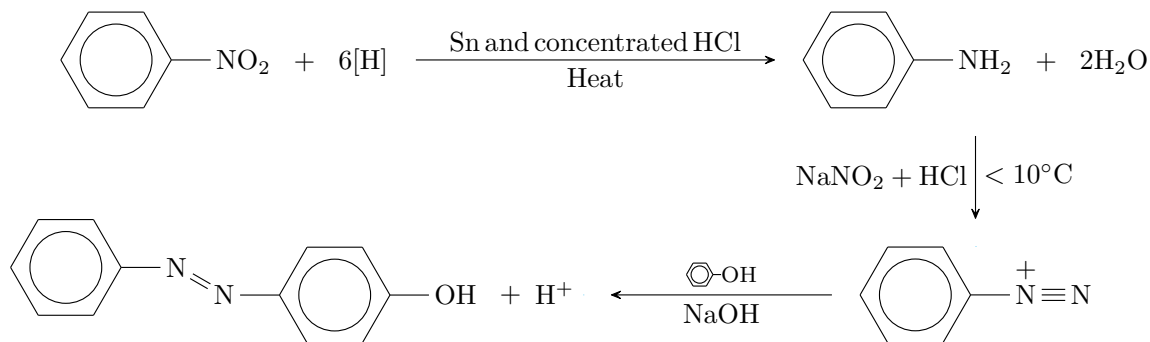


Figure 25.4: Diazonium dye reaction scheme

The product is called a diazonium dye (or azo dye). It is very stable (so colours do not fade), as the delocalised *pi* bonding system extend over between the two aromatic rings through the $-\text{N}=\text{N}-$ ‘bridge’.

25.4 EDG and EWG

EDG: Electron donating group. Normally groups with high electron densities. (Often a highly EN atom attached directly to the benzene ring) These groups push their electron density onto the benzene ring, activating the 2,4,6-positions on the ring. Due to the activation, reaction conditions needed are normally milder when an EDG is attached.

EWG: Electron withdrawing group. Normally groups with low electron densities. (Often a highly EN atom that is indirectly attached can cause this.) These groups deactivate the 2,4,6-positions. Therefore newly attached groups go to the 3,5-positions.

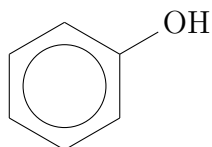
Section 9 of the data booklet contains which groups direct new groups to which positions. Table 25.2 is a copy of that page:

2,4,6-positions	3,5-positions
$-\text{NH}_2$, $-\text{NHR}$, $-\text{NR}_2$	$-\text{NO}_2$
$-\text{OH}$, $-\text{OR}$	$-\text{NH}_3^+$
$-\text{NHCOR}$	$-\text{CN}$
$-\text{CH}_2$, -alkyl	$-\text{CHO}$, $-\text{COR}$
$-\text{Cl}$	$-\text{CO}_2\text{H}$, $-\text{CO}_2\text{R}$

Table 25.2: Common groups attached to benzene with directing effects

25.5 Phenol

25.5.1 Structure



25.5.2 Properties

- White crystalline solid;
- Slightly soluble in water;
- More acidic than water and alcohols; (but not acidic enough to react with CO_3^{2-})
This is because the p-orbitals of O atom in $-\text{OH}$ overlap with the p-orbitals in benzene. The bonding system in benzene attracts the p-orbitals of the O atom. The electron density on the O–H bond is lowered, so the bond is weaker.
- Much more reactive than benzene because the $-\text{OH}$ group is an EDG and activates the 2,4,6-positions.

25.5.3 Reactions






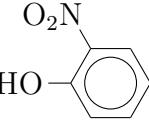

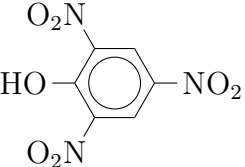
Reactants	Products	Property
HO-  , NaOH	Na ⁺ O ⁻ -  (, H ₂ O)	Acid
HO-  , Na	Na ⁺ O ⁻ -  (, H ₂)	Acid
HO-  , dil. HNO ₃ (r.t.)		Increased reactivity
HO-  , hot HNO ₃		Increased reactivity

Table 25.3: Reactions based on phenol

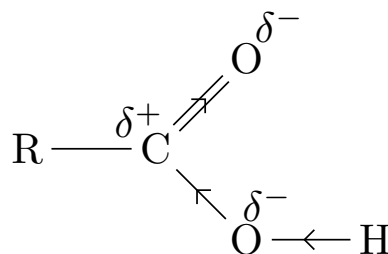
Chapter 26 Carboxylic Acids and Derivatives

26.1 Naming

Structure	Name
$\begin{array}{c} \text{HO} \quad \text{O} \\ \diagdown \quad // \\ \text{C} - \text{C} \\ // \quad \diagdown \\ \text{O} \quad \text{OH} \end{array}$	Ethanedioic acid
$\begin{array}{c} \text{O} \\ // \\ \text{C} - \text{O} - \text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5 \end{array}$	Phenyl benzoate
$\begin{array}{c} \text{O} \\ // \\ \text{CH}_3 - \text{C} - \text{Cl} \\ \\ \text{O} \end{array}$	Ethanoyl chloride
$\begin{array}{c} \text{O} \\ // \\ \text{C} - \text{O} - \text{Cl} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Benzoyl chloride

Table 26.1: Naming of some special carboxylic acids and acyl chlorides

26.2 Structure



Electrons in the C–O bond are drawn towards the C=O bond. Some electron density on the O–H bond is also attracted towards the carboxyl group. This weakens the O–H bond significantly. (H^+ leaves easily.)

Two things can be further deduced:

1. The carboxyl group is an EWG. If a benzene ring is attached to the carboxyl group ($-\text{COOH}$ or $-\text{COOR}$), electrons are withdrawn from the ring to the carboxyl group, **d**eactivating positions 2, 4 and 6.
2. The acidity of the carboxylic acid depends also on the properties of the group R–. If the group is an EDG, the acid is weaker; if the group is an EWG, the acid is stronger (because it adds to the weakening of the O–H bond due to it attracting electron density from the carboxyl group and, consequently, the O–H bond.)

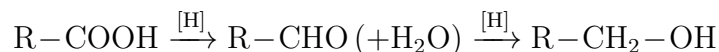
An example for point 2: CH_3-COOH is a stronger acid than $\text{CH}_2\text{Cl}-\text{COOH}$, which is stronger than $\text{CHCl}_2-\text{COOH}$, which is then stronger than CCl_3-COOH . This is because

the Cl atom is highly electronegative and attracts electron density towards it. Therefore CCl_3^- is the most EWG and creates the most strongest carboxylic acid.

26.3 Reactions

26.3.1 Reduction

Use LiAlH_4 (in dry ether). This reduces it to an aldehyde which is then reduced to an alcohol.



26.3.2 Oxidation

Two very special cases:

- Methanoic acid $\text{HCOOH} + [\text{O}] \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$
- Ethanedioic acid $\text{C}_2\text{H}_2\text{O}_4 + [\text{O}] \longrightarrow 2\text{CO}_2 + \text{H}_2\text{O}$. Use strong oxidisers like KMnO_4/H^+

Other carboxylic acids are not easily oxidised.

26.3.3 Esterification

- Condition: conc. H_2SO_4
- Can be seen as condensation reaction (a molecule of water is condensed out)
- Reverse reaction: hydrolysis

26.4 Acyl chlorides

The naming is simple: replace the -ic in the acid and replace with -yl chloride. E.g., CH_3COOH ethanoic acid; CH_3COCl ethanoyl chloride.

26.4.1 Making acyl chloride

Suppose the target acyl chloride is $\text{R}-\text{COCl}$. There are three options, each starting from $\text{R}-\text{COOH}$

- Add PCl_5 . This can be done at room temperature.
- Add SOCl_2 . This can be done at room temperature.
- Add PCl_3 . This is not as reactive, so heating is required.

Observation: White fumes (HCl , which is irritant and corrosive). Therefore the process needs to be carried out in a fume cupboard.

26.4.2 Reactions

Some simple ones are listed in Table 26.2.

Reactant (+ R-COCl)	Product	Note
Alcohol	Ester	Non-reversible
H ₂ O	R-COOH	(Generates HCl white fumes, fume cupboard)
NH ₃	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	Product called alkanamide
R ₁ -NH ₂	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{H}}{\text{N}}-\text{R}_1$	Product called N-alkyl alkanamide
R ₁ -NH-R ₂	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\underset{\text{R}_1}{\text{N}}-\text{R}_2$	Product called N,N-alkyl alkyl alkanamide

Table 26.2: Common reactions based on acyl chlorides

The mechanism for all these reactions are all nucleophilic addition-elimination and they are almost identical to each other. The mechanism is shown below (using water as an example).

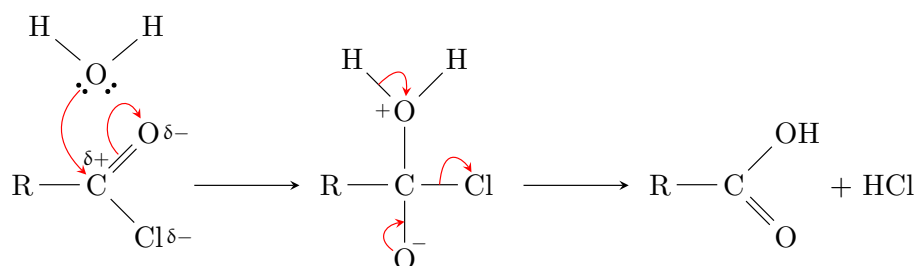


Figure 26.1: Acyl chloride nucleophilic substitution mechanism

If you want to make a phenyl ester, you must react an acyl chloride with a phenoxide salt, as phenol and carboxylic acids do not react.

Chapter 27 Organic Nitrogen Compounds

Three classes of amines²:

- Primary: NH_2R
- Secondary: NHR^1R^2
- Tertiary: $\text{NR}^1\text{R}^2\text{R}^3$
- Quaternary (only for ammonium salts): $^+\text{NR}^1\text{R}^2\text{R}^3\text{R}^4$ (You probably do not need to know this.)

To name amines, there are two options:

- Use the amine as the main functional group;
- Use the alkane chain (or some other higher priority group if applicable) as the main functional group (and use the amino-prefix).

For instance, the amine $\text{CH}_3\text{CH}_2\text{NH}_2$ can be called

- Ethylamine; or
- 1-aminoethane

Note that the latter convention is always to be used as long as there is a higher priority functional group (e.g., a carboxylic acid).

27.1 Physical Properties

1. Short chain amines are soluble in water due to their lone pairs allowing the formation of hydrogen bonding.
Longer chain amines are sparingly soluble, as the longer chain interferes with the hydrogen bonding.
2. Boiling Points: General trend is increase with molecular mass
Primary amines: High boiling point due to hydrogen bonds.
Secondary amines: lower boiling point because alkyl groups decrease the dipole strength.
Tertiary amines: no hydrogen bonding at all, so it has the lowest b.p..

27.2 Basicity of amines


Because amines can be seen as substituted ammonia, they share many similar properties. Basicity is one of them. This is due to the lone pair on the N atom allowing it to accept H^+ by forming a dative covalent bond with it.



In the exam you may be asked to compare the basicity of compounds. You can either check the availability of the lone pair (recommended) or talk about the stability of the conjugate acid by analysing the strength of the N–H bond (not recommended).

An example is given below:

²There is an alternative classification into two classes: aliphatic and aromatic. Aliphatic compounds are those that don't contain aromatic rings.

 -NH ₂	weaker	One of the p-orbitals overlap with the π bonding system in the ring. The electron density is attracted to the π bonding system and the lone pair is less available for forming dative bonds.
C ₂ H ₅ NH ₂	stronger	Alkyl group is an EDG, pushing electron density onto the nitrogen atom, increasing the availability of the lone pair.

27.3 Making amines

Phenylamines have a separate preparation procedure in Section 27.3.4.

Sections 27.3.1 through 27.3.3 are for alkylamines only.

27.3.1 From halogenoalkanes

Basic principle: $\text{RX} + 2\text{NH}_3 \longrightarrow \text{RNH}_2 + \text{HX} + \text{NH}_3 \longrightarrow \text{RNH}_2 + \text{NH}_4^+ + \text{X}^-$.

Conditions: Excess NH₃, heat, under pressure (in sealed tube).

Mechanism: Nucleophilic substitution.

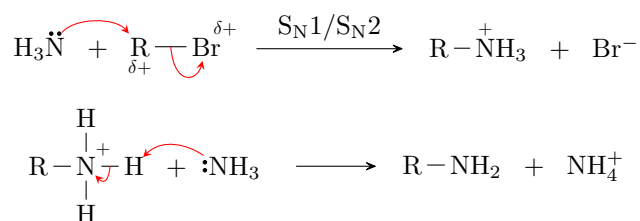
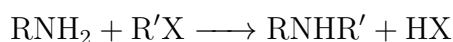
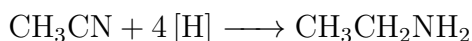


Figure 27.1: Nucleophilic substitution to prepare amines

Further reaction can produce 2°, 3° amines and 4° ammonium salts (e.g., (C₂H₅)₄N⁺Br⁻).

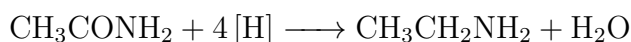


27.3.2 From nitriles



Reducing agent: Ni/H₂, or LiAlH₄ in dry ether.

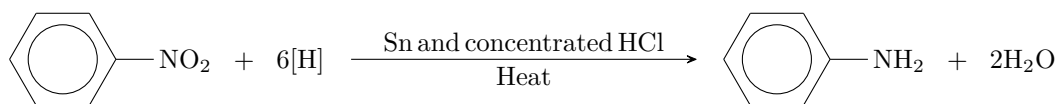
27.3.3 From amides



Reducing agent: LiAlH₄ in dry ether.

27.3.4 Making phenylamine

This is the also the first step in the diazotisation process.



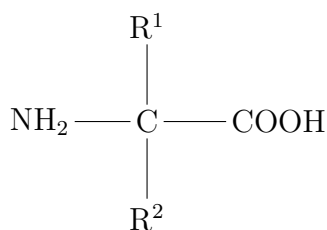
27.4 Reactions of phenylamine

- Mix with bromine water Br_2 (aq). Attaches Br atoms on 2,4,6-positions. Bromine water decolourised and white ppt. This reaction is extremely similar to that of phenol's.
- Diazotisation. See Section 25.3.3.

27.5 Amino acids

27.5.1 Structure

An amino acid has two functional groups: an amine (amino-) group and a carboxylic acid functional group. We only examine α -amino acids, which take the form



where R^1 and R^2 can be H. The α in the name comes from the fact that the amino group is attached to the alpha carbon.

27.5.2 Zwitterion

Amino acids can interact with themselves because it has a basic amino group and an acidic carboxylic acid group. A proton can then transfer from the carboxylic group to the amino group. This gives a dipolar ion which increase intermolecular forces.

In an acidic environment, the amino group changes into an ammonium ion ($-\text{NH}_3^+$); whereas under a basic conditions, the carboxylic acid group is changed to carboxylate ($-\text{COO}^-$). Under a specific pH, the amino acid molecules/zwitterions are (on average) electrically neutral. This pH is called the isoelectric point.

27.5.3 Amide linkages

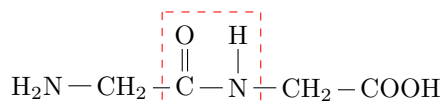


Figure 27.2: Amide linkage

The linkage shown in the red rectangle in Figure 27.2 is the amide linkage. It is also called a peptide linkage when the bond joins two amino acids³.

³This is not accurate, but for A Level it's good enough

If two amino acids join together, it's called a dipeptide.

If three amino acids join together, it's called a tripeptide.

More \rightarrow polypeptide.

Proteins are polypeptides with high molecular mass.

Hydrolysis of peptide linkages (and proteins) is slow in water. In acidic/basic conditions it would be faster and would produce salts.

The bond broken is the C–N bond.

27.5.4 Electrophoresis

A quick search in the syllabus reveals that this is the only place where electrophoresis is actually required.

Electrophoresis is used for separating, identifying and purifying proteins⁴.

Electrophoresis essentially is making ions move by applying an electric field. Different amino acids have different isoelectric points, so they have (on average) different charges. They also have different sizes. The higher the charge and smaller its size, the faster it travels during electrophoresis. The direction depends on the charge on the amino acid (, and consequently, the relation between the environment pH and the isoelectric point).

27.5.5 Making amides

Reacting an acyl chloride with an amine at room temperature is enough, as shown in Figure 27.3.

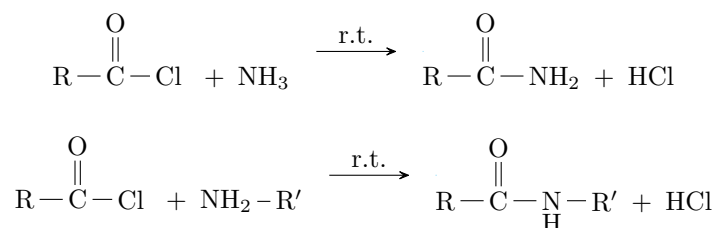


Figure 27.3: Making amides

⁴However, in electrophoresis, the amino acids (from hydrolysing the protein) are responsible for any observations, as they can form ions whereas proteins can't.

Chapter 28 Polymerisation

28.1 Addition polymerisation

Reagent include $C=C$ and $C\equiv C$. The only products formed are polymers.

28.2 Condensation polymerisation

Reactants	Product (one repeat unit)	By-product
$HO_2C-X-CO_2H, HO-Y-OH$	$\begin{array}{c} O \quad O \\ \quad \\ -C-X-C-O-Y-O- \end{array}$	H_2O^*
$HO_2C-X-CO_2H, H_2N-Y-NH_2$	$\begin{array}{c} O \quad O \\ \quad \\ -C-X-C-N-Y-N- \\ \quad \\ H \quad H \end{array}$	H_2O^*
$\begin{array}{c} O \\ \\ HO-X-C-OH \end{array}$	$\begin{array}{c} O \\ \\ -O-X-C- \end{array}$	H_2O^{**}
$\begin{array}{c} O \\ \\ H_2N-X-C-OH \end{array}$	$\begin{array}{c} O \\ \\ -N-X-C- \\ \\ H \end{array}$	H_2O^{**}

Table 28.1: Common condensation polymers.

* HCl would be produced if acyl chlorides were used instead of carboxylic acids.

** You can't really use the acyl chloride for this because they spontaneously polymerise, i.e., they are not stable.

28.3 Disposing of polymers

Condensation polymers consist of amide or ester linkages, which can be hydrolysed and therefore is biodegradable and sometimes photodegradable.

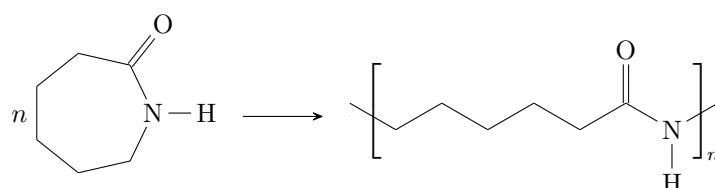
Addition polymers are linked using $C-C$ bonds, which are too strong to be hydrolysed or broken down by biological processes. They can be disposed through combustion, recycling, or burial.

28.4 Notable condensation polymers

28.4.1 Nylon-6,6

This corresponds to case 2 in Table 28.1, where X is $(CH_2)_4$, and Y is $(CH_2)_6$. The two "6"s mean that there are 6 carbons in each monomer.

28.4.2 Nylon-6



This is special, as it uses ring-opening polymerisation.

It is used in ropes and fibers due to its high strength.

28.4.3 Kevlar®

(Apparently I *have to* add the registered trademark symbol?)

This corresponds to case 2 in Table 28.1, where the two monomers are $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$ and $\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$.

Uses: bullet-proof body armour, tennis rackets.

Properties: high strength, resistant to fire. The high strength is caused by two things:

- Hydrogen bonding between chains of Kevlar®;
- Flat structure of benzene ring makes contact area very large, which lead to high London forces.

Chapter 29 Analytical Chemistry

I give up, so here are some little useful things.

29.1 Chromatography

- Partition: separation due to the different solubilities of compounds in two solvents
- Adsorption: separation due to the different attraction between the compounds and the stationary phase, relative to their solubility in the solvent

Type	Principle	Mobile phase	Stationary phase
Paper	Partition	Organic Solvent	Water trapped between fibers of paper
TLC	Adsorption	Nonpolar Solvent	Silica or alumina
HPLC	Partition	Polar solvent	Non-volatile liquid supported on silica
GLC	Partition	Inert gas (like Ar or N ₂)	Non-volatile liquid supported on silica

Table 29.1: Jacob's understanding of chromatography. Cannot guarantee correctness.

29.2 NMR

I don't have anything in particular that I want to mention, so... Meh.

29.3 IR Spectroscopy

I don't have anything in particular that I want to mention, so... Meh.

A2 Chemistry
Revision Notes / Lightweight Textbook
Volume 2. Physical and Inorganic Chemistry

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Revised and transcribed into L^AT_EX by Yunzhi Liu

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Chapter 19 Lattice Energy

19.1 Definition

Lattice Energy: Enthalpy change when 1 mol of an ionic compound is formed from its gaseous ions under standard conditions.

- Always negative / always exothermic. (Bonds form, so energy is released.)

Standard enthalpy change of atomisation $\Delta H_{\text{at}}^\ominus$: The enthalpy change when 1 mol gaseous atoms is formed from its element in the standard state under standard conditions.

1st electron affinity $\Delta H_{\text{ea1}}^\ominus$: The enthalpy change when 1 mol e^- is added to 1 mol gaseous atoms to form 1 mol gaseous 1 $-$ ions under standard conditions.

2nd electron affinity $\Delta H_{\text{ea2}}^\ominus$: The enthalpy change when 1 mol e^- is added to 1 mol gaseous 1 $-$ ions to form 1 mol gaseous 2 $-$ ions.

Enthalpy change of hydration: The enthalpy change when 1 mol gaseous ions dissolves in sufficient water to form an infinitely dilute solution under standard conditions.

Enthalpy change of solution: The enthalpy change when 1 mol of ionic solid dissolves in sufficient water to form an infinitely dilute solution under standard conditions.

19.2 Born-Haber cycle

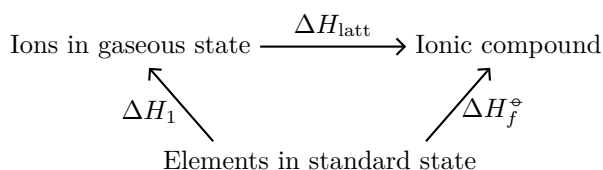
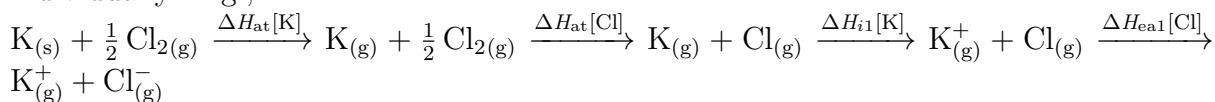


Figure 19.1: A Born-Haber cycle for calculating the lattice energy

Figure 19.1 is a typical cycle for solving for the lattice energy. $\Delta H_f^\ominus = \Delta H_1 + \Delta H_{\text{latt}}$. Note that when supplied with the actual elements, you will need to outline each step individually. E.g.,



Another diagram is the energy level diagram shown in Figure 19.2.

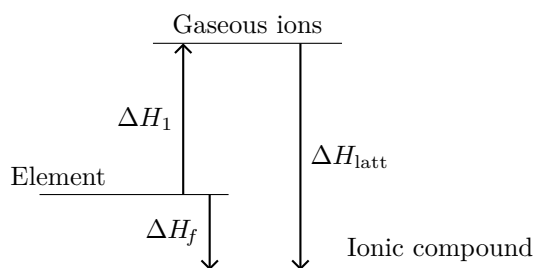


Figure 19.2: Energy level diagram. Pay attention to relative height of energy levels and directions of arrows.

19.3 Factors affecting value of lattice energy

- Size of the ions: smaller size \Rightarrow higher charge density \Rightarrow more exothermic;
- Charge on the ions: higher charge \Rightarrow higher charge density \Rightarrow more exothermic.

19.4 Ion polarisation

Commonly examined in questions about the thermal stability of Group 2 nitrates / carbonates.

Positively charged cations in an ionic lattice attract electrons in anion towards it. This causes a distortion of the electron cloud in the anion, which is no longer in its original spherical shape.

Polarising power: The ability of a cation to attract electron density and distort an anion.

Factors affecting ion polarisation:

- Charge density of cation: higher charge density \Rightarrow more polarised. (Smaller size, higher charge \Rightarrow More powerful)
- How easily the anion can be polarised (Large (polyatomic) anion with high charge \Rightarrow easily polarised)

Thermal stability of Group 2 carbonates and nitrates: thermal stability increases down the group.

- Down the group, the charge of the cation is the same, but the ionic radius increases.
- \Rightarrow The charge density of the cation decreases. The *Rightarrow* The polarising power of the cation decreases.
- \Rightarrow The carbonate ion is less polarised \Rightarrow The C–O bond is weakened less, so the carbonate ion is more stable.

19.5 Solubility of Group 2 Sulfates

Solubility decreases down the group. (Recall that BaSO_4 is famously insoluble even in strong acids.)

$$\Delta H_{\text{sol}}^{\ominus} = \Delta H_{\text{hyd}}^{\ominus} - \Delta H_{\text{latt}}^{\ominus}$$

1. Enthalpy change of hydration becomes less exothermic down the group.
2. Lattice energy becomes less exothermic down the group.
3. The change in hydration energy outweighs the change in lattice energy (i.e., the change in hydration energy is larger)

4. $\Delta H_{\text{sol}}^{\circ}$ gets more endothermic
5. Dissolving is more difficult.

19.6 Solubility of Group 2 Hydroxides

Solubility decreases down the group. (Recall that $\text{Mg}(\text{OH})_2$ is only very slightly soluble; whereas $\text{Ba}(\text{OH})_2$ is a strong base and is very soluble.)

$$\Delta H_{\text{sol}}^{\circ} = \Delta H_{\text{hyd}}^{\circ} - \Delta H_{\text{latt}}^{\circ}$$

1. Enthalpy change of hydration becomes less exothermic down the group.
2. Lattice energy becomes less exothermic down the group.
3. The change in hydration energy is outweighed by the change in lattice energy (i.e., the change in hydration energy is smaller)
4. $\Delta H_{\text{sol}}^{\circ}$ gets more exothermic
5. Dissolving is easier down the group.

Chapter 20 Electrochemistry

20.1 Redox

A mnemonic: OIL RIG. (Oxidation Is Losing e^- ; Reduction Is Gaining e^- .)

If a species is reduced, it is an/the oxidising agent;

If a species is oxidised, it is a/the reducing agent.

20.2 Electrolysis

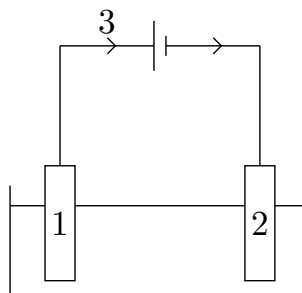
Decomposition of a compound into its elements by an electric current.

The power supply must be a direct current source.

Electrode: rods that conduct electricity to and from the electrolyte. It is always safe to use graphite or platinum (Pt).

- Anode: anions go to the anode. Oxidation takes place here.
- Cathode: cations go to the cathode. Reduction takes place here.

1. Anode. Here anions give their electrons to the circuit and get oxidised to their elemental form.
2. Cathode. Here cations receive electrons from the circuit and are reduced to their elemental form.
3. Arrows represent the direction of flow of electrons.



Examples:

- Conc. $\text{NaCl}_{(\text{aq})}$
 Anode: $2 \text{Cl}^- \longrightarrow \text{Cl}_2 + 2 e^-$, Cl_2 bubbles off.
 Cathode: $2 \text{H}^+ + 2 e^- \longrightarrow \text{H}_2$, H_2 bubbles off.
- Dil. $\text{NaCl}_{(\text{aq})}$
 Anode: $4 \text{OH}^- \longrightarrow 2 \text{H}_2\text{O} + \text{O}_2 + 4 e^-$, O_2 bubbles off.
 Cathode: $2 \text{H}^+ + 2 e^- \longrightarrow \text{H}_2$, H_2 bubbles off.

Faraday constant $F = 96\,500 \text{ C mol}^{-1}$ ($F = e \cdot N_A$)

20.3 Electrode potential

When a metal is put into a solution of its ions, an electric potential is established between the metal and the metal ions. This cannot be directly measured, so we introduce a reference electrode: the standard hydrogen electrode (Figure 20.1). The potentials for all half-cells can be measured relative to this electrode.

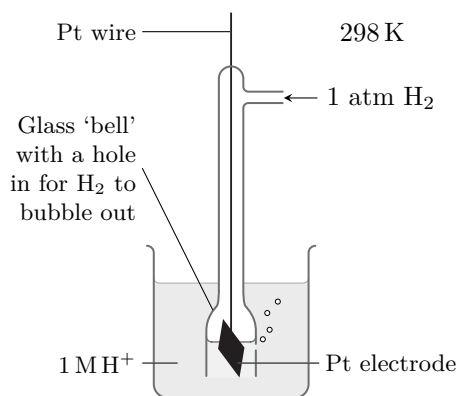


Figure 20.1: Standard Hydrogen Electrode. Note the standard conditions.

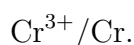
Standard electrode potential: The standard electrode potential (of a half-cell) is the voltage measured under standard conditions with a standard hydrogen electrode as the other half-cell.

20.4 Salt bridge

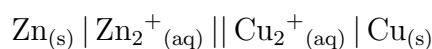
When two half-cells are joined together using a wire, a salt bridge that bridges the two half-cells is needed. This allows movement of ions between the half-cells, thus completing the electrical circuit. Note that the charge carriers in the salt bridge are the ions, not electrons.

20.5 Representing cells

A half-cell is represented (in the textbook) as “X / Y”¹, e.g.,



Our textbook does not use notations for full cells (instead, it simply refers to the two half-cells). However, here is an example of the conventional notation:

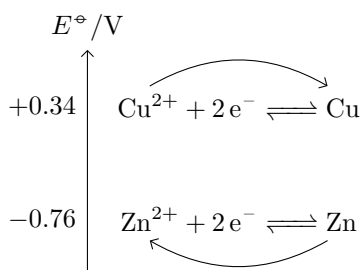


A single vertical line represents a phase boundary (e.g., gas|liquid boundary). The double vertical line represents the salt bridge, (separating the two half cells.)

20.6 Predict how two half-cells will react

In an E° diagram, the reaction happens clockwise, as shown in Figure 20.2. (And electrons flow from the negative to the positive electrode.)

¹There seems to be no rule for which comes first: both Cu^{2+}/Cu and Cu/Cu^{2+} have appeared in the textbook.

Figure 20.2: Example E^\ominus diagram

20.7 The Nerst equation

$$E = E^\ominus + \frac{RT}{nF} \ln \frac{[\text{Ox}]}{[\text{Red}]}$$

$$\stackrel{?}{=} E^\ominus + \frac{0.059}{n} \log [\text{Oxidised form}]$$

where

- E is the electrode potential under non-standard conditions
- E^\ominus is the standard electrode potential
- $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant
- T is the thermodynamic temperature (i.e., temperature given in K)
- n is the number of electrons transferred in the reaction. Our textbook uses z for this. This is always an integer.
- $F = 96\,500 \text{ C mol}^{-1}$ is the Faraday constant.
- The $\stackrel{?}{=}$ assumes: a metal ion / metal electrode², and a standard temperature of 298 K.

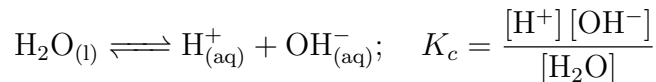
(The section “Cells and Batteries” is not specified in the syllabus, therefore it is omitted from this document.)

²i.e., concentration of the reduced form (the metal) is constant

Chapter 21 Equilibria

21.1 Basic concepts

21.1.1 Ionic product of water K_w



$[\text{H}_2\text{O}]$ is regarded as constant (because the amount dissociated is extremely small). Therefore,

$$K_w = [\text{H}^+][\text{OH}^-]$$

In pure water, since $[\text{H}^+] = [\text{OH}^-]$, $K_w = [\text{H}^+]^2 = [\text{OH}^-]^2$.

21.1.2 pH

$$\text{pH} \stackrel{\text{def}}{=} -\log_{10} [\text{H}^+] \quad [\text{H}^+] = 10^{-\text{pH}}$$

For strong acids, $[\text{H}^+]$ from ionisation of water molecules is very small compared to those arising from the acid.

$$\text{pH} = -\log_{10} [\text{strong acid}]$$

Strong bases

$$[\text{H}^+] = \frac{K_w}{[\text{strong base}]} \Rightarrow \text{pH} = -\log_{10} \left(\frac{K_w}{[\text{strong base}]} \right)$$

For weak acids, we need to define a “Acid dissociation constant” K_a .

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}; \text{p}K_a = -\log_{10} K_a$$

Larger K_a , smaller $\text{p}K_a$, stronger acid.

$$K_a = \frac{[\text{H}^+]^2}{[\text{HA}]}; [\text{H}^+] = \sqrt{K_a \cdot [\text{HA}]} \Rightarrow \text{pH} = -\log_{10} \sqrt{K_a \cdot [\text{HA}]}$$

21.2 Indicators and acid-base titrations

Acid-base indicator: A dye or mixture of dyes that changes colour over a specific pH range. (But why would anyone ask for the definition for this?)

Many indicators can be seen as a weak acid $\text{HIn} \rightleftharpoons \text{H}^+ + \text{In}^-$, where HIn is a different colour from In^- .

Equivalence point: Number of moles of H^+ is equal to that of OH^- . Also called stoichiometric point.

Sharp fall: rapid change in pH value. The indicator should be chosen such that the pH range in which the indicator changes color lies in the sharp fall.

Titration type	Sharp fall pH range
Strong acid + Strong base	3.5 – 10.5
Strong acid + Weak base	3.5 – 7.5
Weak acid + Strong base	7.5 – 11
Weak acid + Weak base	No sharp fall

Table 21.1: Sharp fall pH ranges

TOD0: add pH curves for each case

21.3 Buffer solutions

Buffer solution: A buffer solution is a solution whose pH does not change significantly when small amounts of acid or base are added.

One type of buffer solution is a mixture of a weak acid and one of its salts. Its pH can be calculated using the equation below.

$$\text{pH} = \text{p}K_{\text{a}} + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

Uses of buffer solutions: electroplating, manufacturing dyes, treatment of leather, etc..

21.4 Solubility

Solubility: number of moles of compound needed to saturate 1 dm^3 at 298 K.

Solubility product K_{sp} : product of concentrations of each ion in a saturated solution of a sparingly soluble salt at 298 K, raised to the power of their relative concentrations.

For an ionic compound X_aY_b , its K_{sp} is defined as:

$$K_{\text{sp}} \stackrel{\text{def}}{=} [\text{X}_{(\text{aq})}^{\text{m}+}]^a \cdot [\text{Y}_{(\text{aq})}^{\text{n}-}]^b$$

If compounds are added in a way that causes $[\text{X}_{(\text{aq})}^{\text{m}+}]^a \cdot [\text{Y}_{(\text{aq})}^{\text{n}-}]^b > K_{\text{sp}}$, precipitation will occur until $[\text{X}_{(\text{aq})}^{\text{m}+}]^a \cdot [\text{Y}_{(\text{aq})}^{\text{n}-}]^b \leq K_{\text{sp}}$.

Common ion effect: The reduction in solubility of a dissolved salt by adding a solution of a compound which has an ion in common with the dissolved salt.³ This often results in precipitation.

Partition coefficient: the ratio between concentrations of a solute in two different immiscible solvents when equilibrium has been established.

$$K_{\text{pc}} \stackrel{\text{def}}{=} \frac{[\text{X}_{(\text{Solvent A})}]}{[\text{X}_{(\text{Solvent B})}]}$$

³To help you parse this sentence in case you don't understand: there is no verb in this sentence.

Chapter 22 Reaction Kinetics

22.1 Rate of reaction

$$\text{Rate of reaction} = \frac{\text{change in concentration}}{\text{time taken for this change}} \quad (\text{Unit: mol dm}^{-3} \text{ s}^{-1})$$

Calculating rate graphically: rate = gradient in concentration-time graph.

22.2 Rate equation

$$\text{rate} = k [\text{A}]^m [\text{B}]^n$$

- k : rate constant. Unit depends on $m + n$.
- m, n : order of reaction. The higher the order of reaction, the more influence the corresponding reactant has on the reaction. It is not necessarily a whole number.
- A, B: either reactant or catalyst.

Order of reaction (with respect to a particular reactant/catalyst): the power to which the concentration of that reactant/catalyst is raised in the rate equation.

Half-life $t_{1/2}$: Time taken for the concentration (or mass) of a reactant to fall to half its original value.

Graphs:

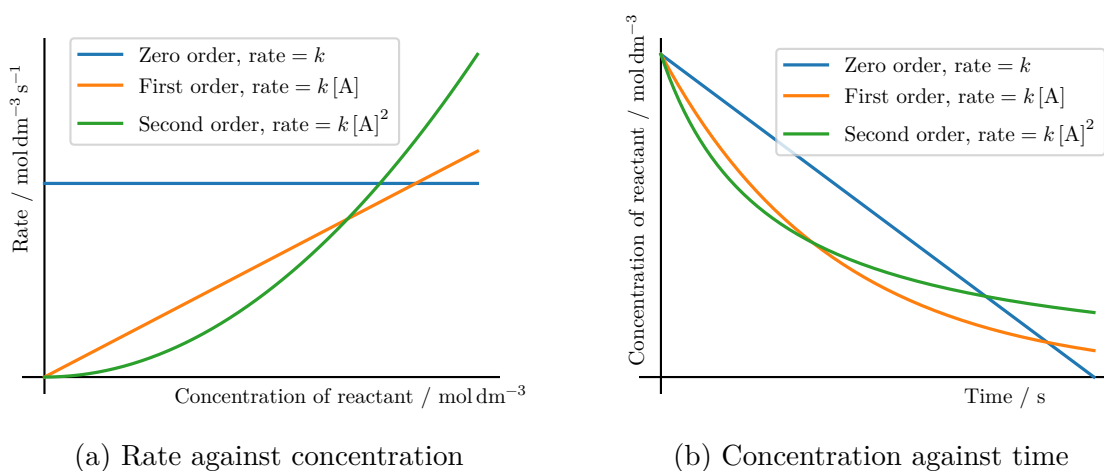


Figure 22.1: Graphs of zero, first and second order reactions

Note that in Figure 22.1b, zero order has a decreasing half-life; first order has a constant half-life; and second order has an increasing half-life.

22.3 Rate-determining step

The slowest step in a mechanism determines the overall rate of reaction. Substances involved in the rate-determining step (probably) occur in the rate equation.

They can therefore be used to verify a proposed mechanism of a reaction.

22.4 Catalysis

22.4.1 Basic concepts

Homogeneous catalysis: catalysis in which the catalyst is the same phase as the reactants

Heterogeneous catalysis: catalysis in which the catalyst is in a different phase from the reactants

22.4.2 Mechanism of heterogeneous catalysis — theory of adsorption

Adsorb: Bond to the surface of a substance

Absorb: Move *into* the substance

Example: iron in Haber process $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$

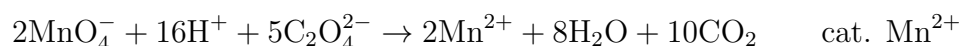
1. **Diffusion:** gas diffuses to the solid surface.
2. **Adsorption:** bonds formed between reactant molecules and the catalyst. The bonds are strong enough to weaken covalent bonds in molecules so they can react, and weak enough to break and allow the product to leave the surface.
3. Reaction
4. **Desorption:** bonds between product and catalyst surface weaken and break.
5. **Diffusion:** product diffuses away from the surface.

Catalyst poisoning: Impurities in the reaction mixture may adsorb onto the surface of the catalyst. The catalyst is then unable to facilitate the reaction.

Transition metals (Platinum Pt, Rhodium Rh, Palladium Pd) in catalytic converters also use this mechanism.

22.5 Autocatalysis

Autocatalysis: occurs when the product of a reaction can act as the catalyst for that reaction. E.g.



Chapter 23 Entropy

23.1 Entropy

Entropy: a measure of dispersal of energy at a specific temperature, or a measure of randomness or disorder of a system.

23.1.1 Comparing entropy values

Standard molar entropy S^\ominus : entropy of one mole of substance in its standard state and under standard conditions. Unit: $\text{J K}^{-1} \text{mol}^{-1}$. All S^\ominus are positive.

Gases in general have much higher entropy than liquids. Liquids in general have higher entropy than solids.

This is frequently examined in the form of “predict whether the entropy change of this reaction is positive or negative” — the answer is whichever side has more moles of gas has the higher entropy.

23.1.2 Calculating entropy changes

The textbook talks extensively about $\Delta S^\ominus_{\text{total}} = \Delta S^\ominus_{\text{system}} + \Delta S^\ominus_{\text{surroundings}}$ and how it can predict the feasibility of a reaction.

However, the syllabus *explicitly* states that this is *not required*, and what we do need to know is $\Delta S^\ominus = \sum_{\text{products}} S^\ominus - \sum_{\text{reactants}} S^\ominus$. I.e., the entropy change of a reaction is the difference between the sum of entropies of products and that of reactants.

The more positive the entropy change, the more likely that the reaction is feasible.

23.1.3 Gibbs Free Energy

When determining whether a chemical reaction is likely to be spontaneous, we use Gibb’s free energy.

For a reaction with enthalpy change ΔH and entropy change ΔS carried out at thermodynamic temperature T , its change in Gibb’s free energy ΔG is given by

$$\Delta G = \Delta H - T\Delta S$$

The reaction is spontaneous only if $\Delta G < 0$.

Note that ΔG depends on temperature. Changes in temperature can affect the spontaneity of the reaction.

Table 23.1 shows which reactions are feasible under what conditions.

		ΔH	
		Positive	Negative
ΔS	Positive	Feasible when hot	Always
	Negative	Never	Feasible when cold

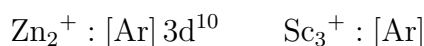
Table 23.1: Table of reaction feasibility

Chapter 24 Transition Elements

24.1 Basic concepts

Transition element: A transition element is a d-block element that forms one or more stable ions with incomplete d orbitals.

Zn and Sc, although are d-block elements, are not transition elements. This is because their ions have either do not have a d orbital, or has a full d subshell.



Transitions elements can exhibit various oxidation states and form complex ions. They have variable oxidation states because 4s and 3d electrons have similar energies. (removing extra electrons do not cost too much more energy)

Note: When Period 4 d-block elements (Sc to Zn) form ions, the 4s electrons are lost first.

24.2 Physical properties

The syllabus does not specify these in the A2 part, but it's commonsense so it can't hurt to know these properties.

- High melting point
- High density
- Hard and rigid
- Good conductor (both electrical and thermal)

24.3 Other properties

These properties are specified by the syllabus, unless explicitly stated otherwise.

24.3.1 Behave as catalysts

They have a partially filled d-orbital. This means they can be used to form bonds with adsorbed reactants which helps the reaction to take place more easily.

24.3.2 Form coloured compounds

Ligands around the central metal ion splits its d-orbitals to give non-degenerate orbitals. This causes an energy gap between d-orbitals. Electrons can absorb light of specific frequencies and get excited to the higher energy level state. The light not absorbed is observed.

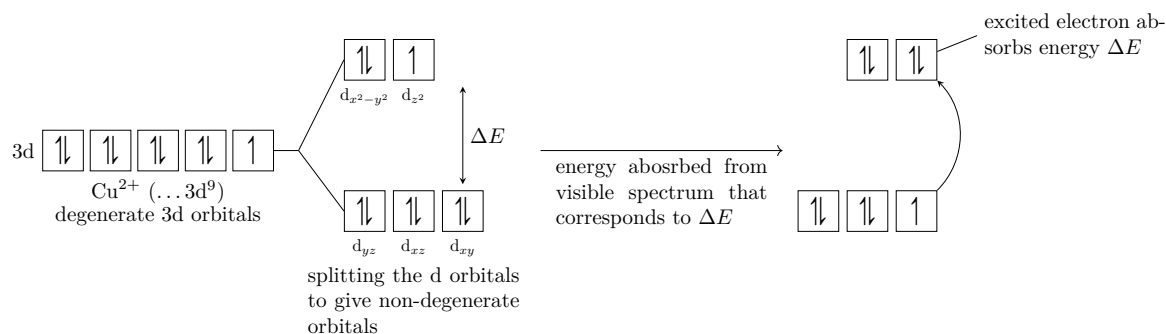


Figure 24.1: Example of splitting of 3d orbitals

24.4 Ligands and complex formation

24.4.1 Basic concepts

Ligand: molecule or ion that bonds to metal by donating its electron pair to form a coordinate bond.

Monodentate Ligand: molecule or ion that bonds to metal by donating one electron pair to form one coordinate bond.

Bidentate Ligand: molecule or ion that bonds to metal by donating two electron pairs to form two coordinate bonds.

Polydentate Ligand: molecule or ion that bonds to metal by donating two electron pairs to form two coordinate bonds.

Complex: Metal ion with coordinately bonded ligands.

Coordinate number: The number of coordinate bonds from the ligands to the central ion.

24.4.2 Ligand shape and isomers

Coordination number 6: octahedral.

Coordination number 4: tetrahedral or square planar. There is “no easy way of predicting that [the square planar structure] is going to happen”⁴.

Coordination number 2: linear

Geometric isomers: Figures 24.2 and 24.3



Figure 24.2: Square planar: cis- and trans- platin

⁴Quoted from [Chemguide: https://www.chemguide.co.uk/inorganic/complexions/shapes.html](https://www.chemguide.co.uk/inorganic/complexions/shapes.html).



(a) cis-tetraamminedichlorocobalt(III)

(b) trans-tetraamminedichlorocobalt(III)

Figure 24.3: Octahedral: cis- and trans-tetraamminedichlorocobalt(III)⁵

Optical isomers: Figure 24.4

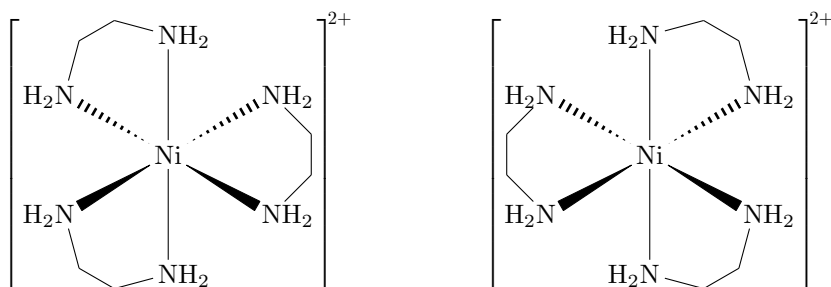


Figure 24.4: Optical isomers: Tris(ethylenediamine)nickel(II)

24.4.3 Colours of common complex ions

Why different complexes have different colours: Different ligands split the d-orbitals differently (ΔE in Figure 24.1 below different), causing different wavelengths of light being absorbed and therefore the complex exhibits a different colour. (See Figure 24.1)

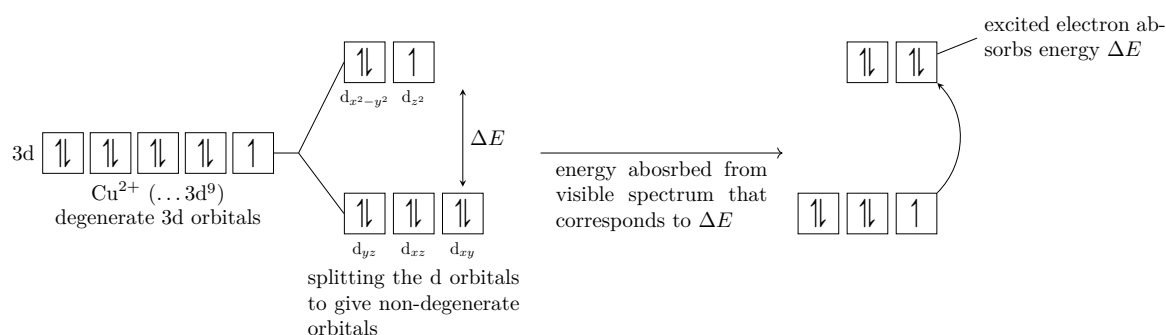


Figure 24.1: Splitting of 3d orbitals in a complex (repeated from page 15)

Colours of common ligands is shown in a table below.

⁵It is not a typo. *Ammine* is the name when ammonia appears as a coordinately bonded ligand.

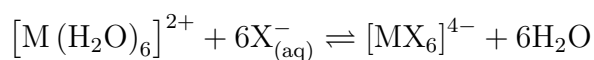
Ligand	Cu (II)		Co (II)	
	Complex	Colour	Complex	Colour
H ₂ O	[Cu (H ₂ O) ₆] ²⁺	Blue	[Co (H ₂ O) ₆] ²⁺	Pink
NH ₃ (drops)	Cu (H ₂ O) ₄ (OH) ₂	Pale blue ppt.	Co (H ₂ O) ₄ (OH) ₂	
NH ₃ (excess)	[Cu (NH ₃) ₄ (H ₂ O) ₂] ²⁺	Deep blue	[Co (NH ₃) ₆] ²⁺	Brown
OH ⁻	Cu (H ₂ O) ₄ (OH) ₂	Pale blue ppt.	Co (H ₂ O) ₄ (OH) ₂	
Cl ⁻	[CuCl ₄] ²⁻	Yellow	[CoCl ₄] ²⁻	Blue

Table 24.1: Table of Copper(II) and Cobalt(II) complexes and their colours

24.4.4 Stability constant K_{stab}

K_{stab} of a complex ion is the equilibrium constant for the formation of the complex in a solvent from its constituent ions.

E.g.,

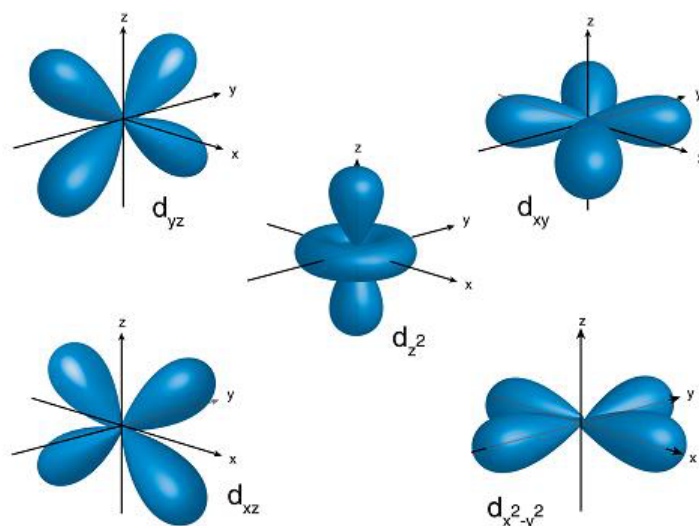


$$K_{\text{stab}} = \frac{[\text{MX}_6]^{4-}}{[\text{M}(\text{H}_2\text{O})_6]^{2+} \cdot [\text{X}^-]^6}$$

water is not included as it is regarded as constant.

Larger K_{stab} means the complex is more stable.

24.4.5 Shape of 3d-orbitals

Figure 24.5: Shape of the degenerate 3d orbitals.⁶

⁶This is the only bitmap image in this whole document. (Mainly because my math sucks and don't know the equations for those surfaces. FML.)

The end