Atomic Structure – Additional Mass Spectrometry

• Working out Atomic Mass from Isotopes
  • \( \text{Ar of X} = \frac{\text{sum of } (m/z \times \text{relative abundance})}{\text{sum of relative abundance}} \)
  • \( \text{Ar of Mg} = \frac{(24 \times 79.0) + (25 \times 10.0) + (26 \times 11.0)}{79.0 + 10.0 + 11.0} = 24.3 \)

• Relative Molecular Mass (Mr)
  • “the mean mass of a molecule compared to one-twelfth of a 12C atom”

• Zirconium Mass Spec:
  
So, Mr is 96, Base Peak is 90
Atomic Structure – Electron Configurations of Ions

• The S and P Blocks
  • For +1 Ions
    • Calcium (11) = 1s² 2s² 2p⁶ 3s¹
    • Calcium⁺ (10) = 1s² 2s² 2p⁶
  • For +2 Ions
    • Magnesium (12) = 1s² 2s² 2p⁶ 3s²
    • Magnesium²⁺ (10) = 1s² 2s² 2p⁶
  • For +3 Ions
    • Aluminium (13) = 1s² 2s² 2p⁶ 3s² 3p¹
    • Aluminium³⁺ (10) = 1s² 2s² 2p⁶
• They have all become isoelectronic with Neon (10) = 1s² 2s² 2p⁶

• The D Block
  • We take from the 4s first
    • Chromium (24) = [Ar] 3d⁵ 4s¹
    • Chromium³⁺ (21) = [Ar] 3d³
    • Iron (26) = [Ar] 3d⁶ 4s²
    • Iron²⁺ (24) = [Ar] 3d⁶

• Non metal Ions
  • We give to the highest energy level first
    • Phosphorous (15) = 1s² 2s² 2p⁶ 3s² 3p³
    • Phosphorous³⁻ (18) = 1s² 2s² 2p⁶ 3s² 3p⁶
    • Phosphorous as become isoelectronic with Argon (18) = 1s² 2s² 2p⁶ 3s⁶
Amount of Substance – Amount of Substance

- The Mole (the Avogadro Constant)
  - “the number of atoms in 1 gram of any given substance relative to 1/12 of 12C”
  - $6.023 \times 10^{23}$

- $n \text{ (mol)} = \text{mass (g)} / \text{amu}$
  - What is the mass of 3 mol of Helium atoms?
    - $mass = \text{amu} \times n$
    - $mass = 4.0 \times 3$
    - $mass = 12 \text{ grams}$
Amount of Substance – Acid-Base Titrations

• How to do Acid-Base Titration Questions:
  1. Write the Balanced Equation
  2. Underline the (two) substances involved in the question
  3. Write down the information of each substance beneath it
  4. Use the information to find the number of moles
  5. Use the ratio in the equation to find the number of moles for the other underlined substance
  6. Then find the mass with the answer to (5.)

Acid-Base Titration Example:

25.0 cm³ of NaOH is neutralised by 22.5 cm³ of HCl at 0.10 mol dm⁻³.

What was the concentration of NaOH?

1. HCl + NaOH → NaCl + H₂O
2. HCl + NaOH → NaCl + H₂O
3. \( \frac{22.5}{25.0} \) 0.10 mol dm⁻³
4. 0.10 * \( \frac{22.5}{1000} \) = 2.24 * 10⁻³
5. 1:1, so no change
Bonding and Periodicity - Permanent Dipole

- Dipole Attraction
  - When two atoms in a covalent bond have different electronegativities

- Hydrogen Bonds
  - Will happen if:
    - A molecule contains a hydrogen atom covalently bonded to F, O or N
    - There is also a lone pair on the FON atom

- The Structure of Ice
  - Ice has a regular open lattice
  - Further apart in solid than liquid so it expands
  - This is because the water forms hydrogen bonds
Calculating Enthalpy Changes Example:

• Calculate the enthalpy change for the reaction below using the data given.

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O} \]

\[ \Delta H_{c\theta} \text{C}: \quad \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad (-394 \text{ kJ mol}^{-1}) \]

\[ \Delta H_{c\theta} \text{H}_2: \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \quad (-286 \text{ kJ mol}^{-1}) \]

\[ \Delta H_{f\theta} \text{C}_2\text{H}_5\text{OH}: \quad 2\text{C} + 3\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \quad (-278 \text{ kJ mol}^{-1}) \]

\[ \Delta H_{r\theta} = -[\Delta H_{c\theta} \text{C}_2\text{H}_5\text{OH}] + [2\Delta H_{c\theta} \text{C} + 3\Delta H_{c\theta} \text{H}_2] \]

\[ \Delta H_{r\theta} = -[-278] + [2(-394) + 3(-286)] \]

\[ \Delta H_{r\theta} = -[-278] + [-1646] \]

\[ \Delta H_{r\theta} = -1368 \text{ kJ mol}^{-1} \]
Kinetics – Catalysis

• Catalyst
  • "Provides an alternate pathway of lower activation energy"

• Heterogeneous Catalyst
  • In a different phase from the reactants
  • E.g. Hardening of Vegetable Oils (Nickel Catalyst)

• Homogenous Catalyst
  • In the same phase as the reactants
  • E.g. The Ozone (Cl•)
    • Cl• + O₃ → ClO• + O₂
    • ClO• + O₃ → Cl• + 2O₂
  • The Cl• is reproduced again and goes on to destroy more Ozone
Redox Reactions – Combining Half-Equation

How to combine Half equations

1. Write out the two half-equations
2. Note the number of electrons each half equation gains or loses
3. Multiply the half equations to get the electrons to equal values
4. Combine the equations by putting all the reactants on one side and all the products on the other
5. Cancel the electrons to get the final equation

(A) $Fe^3+ + e^- \rightarrow Fe^{2+}$, (B) $Zn \rightarrow Zn^{2+} + 2e^-$

1. Done
2. We need to multiple A by 2
3. (A) $2Fe^3+ + 2e^- \rightarrow 2Fe^{2+}$
4. $2Fe^3+ + 2e^- + Zn \rightarrow 2Fe^{2+} + Zn^{2+} + 2e^-$
5. $2Fe^3+ + Zn \rightarrow 2Fe^{2+} + Zn^{2+}$
Group 2 – Sulphates

- Solubility decreases as you go down Group 2
- Barium Sulphate
  - Barium Sulphate is very insoluble in water (as it’s at the bottom of gp. 2)
  - It is also opaque to X-rays and so can be used as a contrast medium in scans of the digestive system
- Is also used in rat poison
  - $\text{BaCO}_3(s) + 2\text{HCl}(aq) \rightarrow \text{BaCl}_2(aq) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$

Testing for sulphates

- Because Barium Sulphate is insoluble it has become the basis for a laboratory test
- If an unknown solution contains sulphate ions then when it’s added to Barium Chloride/Nitrate, a white precipitate forms
  - $\text{BaCl}_2(aq) + \text{Na}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{NaCl}(aq)$
  - This can be simplified to the ionic equation:
    - $\text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(aq)$
- We must first acidify the test sample with Hydrochloric acid or Nitric Acid
  - This is to prevent the false detection of sulphite ions
    - $2\text{H}^+(aq) + \text{SO}_3^{2-}(aq) \rightarrow \text{SO}_2(aq) + \text{H}_2\text{O}(l)$
Metal Extraction – Acid Mine Drainage

• Acid Mine Drainage
  • Pumps are needed to stop underground mines from flooding
  • When the mine is used and finished with the pumps are taken away
  • The mine floods, oxidising sulphides to $\text{H}_2\text{SO}_4$ which dissolves potentially toxic metals, e.g. iron
  • This produces Fe$^{2+}$ and Fe$^{3+}$ which ruins rivers and coats fish gills
  • It can be stopped with:
    • Calcium Carbonate – to neutralise the acid
    • Reed beds – to reduce the $\text{H}_2\text{SO}_4$ to Hydrogen Sulphide (with its bacteria)
  • This reacts with the metals ions to form insoluble sulphide minerals again
Haloalkanes – The Ozone Layer

• Ozone, O₃ is an allotrope of Carbon

• Reactions in the Ozone Layer
  • With UV light: O₂ → •O• + •O•
  • They can react with oxygen: •O• + O₂ → O₃
  • Ozone can dissociate with UV: O₃ → O₂ + •O•
  • (Decomposition = Production) of Ozone

• CFC’s and the Ozone Layer
  • Each chlorine molecule can decompose 1000’s
    • CCl₃F → •CCl₂F + •Cl
    • •Cl + O₃ → ClO• + O₂
    • ClO• + O₃ → 2O₂ + •Cl

• Repairing the Ozone Layer
  • Nitrogen Monoxide catalyses Ozone Decomp.
    • NO + O₃ → NO₂ + O₂
    • NO₂ + O → NO + O₂
  • CFC’s have been banned as of 1987 in most countries

• Alternatives
  • Hydrochlorofluorocarbons (HCFC’s)
  • Hydrofluorocarbons are chlorine free
Haloalkanes – OH- with Bromoethane

• OH- with Bromoethane (Substitution):
Haloalkanes – CN- with Bromoethane

- CN- with Bromoethane (Substitution):
Alkenes – Haloalkanes from Alkenes

- Electrophiles
  - Accept pairs of electrons
  - Positively charged ions (e.g. H+)
  - Atoms that have a partial positive charge (attached to a largely electronegative atom)

- Electrophilic Addition Reactions
  - Hydrogen Bromide (HBr)
    - $\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br}$
  - Bromine (Br$_2$)
    - $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \rightarrow \text{BrCH}_3\text{CHBr}$
  - Sulphuric Acid
    - $\text{CH}_2=\text{CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$

- (see mechanisms)
Alcohols – Oxidising Alcohols

• Primary Alcohols
  • Primary Alcohols $\rightarrow$ Oxi. $\rightarrow$ Aldehydes
  • Ethanol $\rightarrow$ Ethanal
    • $\text{CH}_3\text{CH}_2\text{OH} + [\text{O}] \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$
  • If the Acidified Potassium Dichromate is in excess then it further oxidises to Carboxylic Acid
    • Ethanal $\rightarrow$ Ethanoic Acid
    • $\text{CH}_3\text{CHO} + [\text{O}] \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$
  • We prevent further oxidation by distilling the aldehyde as the reaction proceeds (removing the aldehyde from the oxidising agent)

• Secondary Alcohols
  • Secondary Alcohols $\rightarrow$ Oxi. $\rightarrow$ Ketones
    • Propan-2-ol $\rightarrow$ Propanone
      • $\text{CH}_3\text{CH}($OH$)$CH$_3$ + [O] $\rightarrow$ CH$_3$COCH$_3$ + H$_2$O

• Tertiary Alcohols
  • Tertiary Alcohols $\rightarrow$ Oxi. $\rightarrow$ No change
    • It can’t oxidise because the R group has no Hydrogen and Oxygen to be taken, only Oxygen
# Alcohols – Distinguishing the Three Types of Alcohol

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Acidified Potassium Dichromate (VI)</th>
<th>Product of Reaction with APD(VI)</th>
<th>Result of testing Product with:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary</td>
<td>Orange (\rightarrow) Green</td>
<td>Aldehyde</td>
<td>Silver Mirror Forms</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Brick-Red Ppt</td>
</tr>
<tr>
<td>Secondary</td>
<td>Orange (\rightarrow) Green</td>
<td>Ketone</td>
<td>No Change</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No Change</td>
</tr>
<tr>
<td>Tertiary</td>
<td>No Change</td>
<td>None</td>
<td>No Change</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>No Change</td>
</tr>
</tbody>
</table>
Analytical Techniques – Using Infrared Spectroscopy

- **Identifying Functional Groups**
  - **Alkanes**
    - C-H bonds
    - C-C bonds
  - **Alkenes**
    - C-H bonds
    - C-C bonds
    - C=C bonds
  - **Carboxylic Acids**
    - C=O
    - O-H
  - **Aldehyde**
    - C=O
  - **Ethers**
    - C-O
  - **Alcohols**
    - O-H bonds
    - H bonds cause the trough to be deep and wide

- **Impurities**
  - Can be identified due to absorption bands that should not be there

<table>
<thead>
<tr>
<th>Bond</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>2850 – 3300</td>
</tr>
<tr>
<td>C-C</td>
<td>750 – 1100</td>
</tr>
<tr>
<td>C=C</td>
<td>1620 – 1680</td>
</tr>
<tr>
<td>C=O</td>
<td>1680 – 1750</td>
</tr>
<tr>
<td>C-O</td>
<td>1000 – 1300</td>
</tr>
<tr>
<td>O-H (alco)</td>
<td>3230 – 3550</td>
</tr>
<tr>
<td>O-H (acid)</td>
<td>2500 - 3000</td>
</tr>
</tbody>
</table>