Lecture 8: Electron Configurations in Many-Electron Atoms

Lecture 9: Atomic Spectroscopy
- Identifying Atoms from their Spectra
- Atomic Absorption Spectroscopy.
- X-Ray Spectroscopy

Lecture 10: Properties of Materials
- Colour, Conductivity, Mechanical Properties
Structure of the Periodic Table

The periodic table can be regarded in terms of electron configurations, denoted by orbital angular momentum quantum number. The periodic table may thus be divided into s, p, d, and f blocks according to which orbital is being filled.

The s-block is 2 electrons “wide”, p-block is 6 (3 p-orbitals x 2 electron/orbital), d-block is 10 (5x2), and the f-block is 14 (2x7).
1. Atomic Radius

The atomic radius is determined by the electronic configuration, and particularly by how far the electron density extends from the nucleus. The wavefunctions and potential energy help make sense of the observed trends.

- **Down a group** the radius increases as an entire new shell of electrons is added each new row. This effect is especially noticeable in going up one atomic number from group 8 (noble gas) to the group 1 (alkali metal). The one additional electron goes into the next s-orbital, increasing the radius markedly.

- **Across a row** the radius decreases as the nuclear charge increases. Electrons are added to orbitals in the same shell (same $n$), so orbital contraction arises mainly from the increased attraction of the nucleus. E.g. the radius shrinks from group 1 to group 2, where both outer shell electrons are in the same $ns$ orbital.
1. Atomic Radius

Radius increases down a group as electrons add to new “shells.”

Across a row the radius decreases as the nuclear charge increases.

From group 8 (noble gas) to the group 1 (alkali metal). The one additional electron goes into the next s-orbital, increasing the radius markedly.

Radii of the s- and p-block elements
2. Ionization Energy

Quantum theory also helps make sense of ionization energy trends.

Stepping down a group, the outer electrons of each element is another shell further away from the nucleus. Inner electrons screen the nuclear attraction that binds the electron, so ionization becomes easier.

Across a row, electrons are added to the same shell. The increase in nuclear charge without additional screening holds the electrons more tightly to the nucleus.

He = 2400 kJ mol⁻¹
3. Electron Affinity (EA)

The electron affinity is like ionization energy. It is the energy required to add an electron to a neutral atom in the gas phase.

The general trends in EA are hard to discern.

We expect EA to decrease in magnitude (less negative) down a group as we move further from the nucleus. Only observed for Groups 1 and 8, or elements after Ne.

We expect EA to increase (more negative) across a row as the nuclear charge increases and size decreases. There are plenty of exceptions to this.
3. Electron Affinity (EA)

Adding an electron is more sensitive to detailed electron configurations than ionization energy or atomic radius. This is evident in the behaviour within some groups.

- Group 8 elements have closed shell configurations and **positive** EA’s, so they do not form anions.

- Groups 6 and 7 have large, negative EA’s, and readily form anions.

- Groups 1 & 2 do not form anions easily. A second electron can be added to Group 1 \((ns^1)\) more easily than Group 2 \((ns^2)\), which has a positive EA.

- Subtle effects in groups 3-5 arise from electron-electron and “spin pairing” interactions – not part of this course.
We have already seen that the set of allowed energies corresponding to solutions of the wavefunction or electronic states for an atom are uniquely determined by its chemical character:

- nuclear charge or atomic number
- electronic configuration

This also means that the set of allowed energy differences between states is unique to each element.

Spectroscopy probes the energy differences between allowed states, from which we can deduce the identity of the atom in two ways:

- Precise $\Delta E$ or wavelength measurements
- Measurements of multiple wavelengths

\[
\Delta E = \frac{hc}{\lambda}
\]
Spectroscopic measurements can be divided into two broad classes.

An electronic transition occurs when an electron changes from one allowed state to another.

The orbital it is *leaving* must be partly filled (it contains at least one electron), and the orbital it is *entering* must be partly unfilled (it contains less than two electrons).

- **Absorption or Absorbance**
  An electron absorbs the energy of a photon, and jumps from a lower into a higher energy orbital.

- **Emission**
  An electron jumps from a higher into a lower orbital, and releases (emits) a photon of energy equal to the difference.
Dispersion Spectrophotometry

The principle of dispersion spectrophotometry is to take a light source that produces a broad, continuous spectrum (a “white source”), and then select and scan through the available range of wavelengths from the source.

Individual wavelengths (monochromatic light) are selected with a monochromator. A monochromator uses the interference of waves to select a very narrow band of wavelengths.

Conceptually, this is like dispersing white light through a prism, and then selecting a particular wavelength from its position in the resulting spectrum (rainbow).
Absorbance Spectrometry

A sample is placed between a light source and a detector. If a particular wavelength of light promotes the electron into an excited state, then that wavelength is absorbed and does not appear (or appears at a reduced intensity) in the detected spectrum.

The attenuation of a beam by absorbance is typically represented in two ways.

- Fraction or Percent Transmission.
- Absorbance
Transmission and Absorbance

Transmission, $T$, is simply defined as the fraction of light that reaches a detector after passing through a sample

$$T = \frac{I}{I_0} \quad \text{and} \quad \%T = 100 \frac{I}{I_0}$$

where $I$ denotes intensity, and $I_0$ is the intensity of a reference beam (no sample present).

Absorbance, $A$, is a logarithmic scale that increases as the transmission decreases.

$$A = \log_{10}\left(\frac{I_0}{I}\right)$$

**Worked Example:** What is the absorbance of a sample with a 1.0% transmission?

$$\%T = 1.0 \Rightarrow \frac{I}{I_0} = 0.010 \text{ or } \frac{I_0}{I} = 100. \quad A = \log_{10}(100) = 2.0$$
AAS was developed in the 1950’s by Dr. Alan Walsh of the CSIRO Division of Chemical Physics. It uses the narrow atomic absorbance lines to uniquely identify and measure the concentrations of atoms in a sample that may contain a complex mixture.

Each element is measured separately by a hollow cathode lamp that uses the same element to produce emission lines with its own unique wavelengths. In this way one element can be singled out of many.

The hollow cathode lamp works like a cathode ray tube. An electrical discharge is used to ionize gaseous atoms (+ve), which then impact onto a metal cathode (-ve). The metal is vaporised and electronically excited, and hence emits its characteristic wavelengths when it returns to its ground state.

For more see http://www.chem.vt.edu/chem-ed/spec/atomic/aa.html
Atomic Absorbance Spectrophotometry (AAS)

Samples for AAS analysis must be vapourised and atomised, so that they are not present as molecules or strongly interacting with other atoms or molecules, as these affect the electronic energy levels and hence the transition wavelengths. This is achieved in two ways.

1. Flame. Flame atomization heats the sample to ~1000°C, which can vapourise solutions. Flame atomisers typically use a vacuum aspirator to suck solution with the element to be analysed into a slit flame (~5cm long).

2. Graphite Furnace. A graphite furnace can work with solid or liquid samples, and smaller volumes than a flame. They also provide a better controlled environment. E.g. the furnace can be oxygen-free to prevent oxidation of the element of interest.

AAS is used quantitatively, to measure the concentration of one or more elements using the appropriate lamp.
Trace Analysis of Elements by AAS

The concentration of an element in a sample can be determined from its absorbance by comparing with one or more standard solutions. This uses Beer-Lambert Law, that absorbance, $A$, is directly proportional to the optical path length, $l$, and concentration, $c$.

$$A = \varepsilon cl$$

The constant of proportionality is a property of the element being examined, and is called the extinction coefficient. In practice, $\varepsilon$ is determined by calibrating the instrument with one or more standard solutions.
Applications of AAS

Flame AAS is routinely used to determine the concentrations of metals in particular in various water environments, and whether these exceed safe levels. E.g. The US Environmental Protection Agency limits lead in drinking water to a maximum of 15 parts per billion (ppb).

1 part per million (ppm) = 1 mg/kg  
1 ppb = 1 mg/1000kg.

Worked Example: Is the concentration of lead in a water sample with absorbance \( A = 0.0068 \) within safe (US) limits? A reference 0.100 ppm standard solution has an absorbance of 0.165.

We are not given the path length, so we treat the product \( \varepsilon l \) as a constant.  
Single-point calibration. For the standard: \( \varepsilon l = A/c = 0.165/0.10\text{ppm} = 1.65\text{ppm}^{-1} \)

For the unknown, \( c = A/\varepsilon l = 0.0068/1.65 = \text{0.0041 ppm or 4.1 ppb} \).
Applications of AAS

AAS can be used to in studies of toxicity, again particularly for heavy metals. Heavy metals like mercury, arsenic, lead, and chromium are not easily stored within the body, so they accumulate in the hair and fingernails. These can be prepared for flame AAS analysis by digestion in concentrated acid, or combusted in an oven.

Samples of the hair and fingernails were taken from the body of the arctic explorer Charles Hall, who died under mysterious circumstances on an expedition in 1871.

The fingernail was found to have 24.6 ppm As at its tip, but 76.7 ppm As at its base. Similar results were found for the hair, suggesting that he had been given a massive dose of the poison in the last two weeks of his life.
Spectra of Stars

Stars emit a broad (so-called “black-body”) spectrum of radiation that depends on their temperature. Higher temperatures shift this emission spectrum towards shorter wavelengths.

Elements (atoms and ions) in the star absorb certain wavelengths, leading to a pattern of dark lines in the continuous spectrum.

These *Fraunhofer Lines* can be used to deduce both the identity and relative concentration of the various elements present.

(This is how we can establish that our sun contains elements heavier than He. (Lecture 2))
Composition of the Sun

The expanded solar spectrum shown below includes series of absorbance lines from many elements.

### Solar Elemental Abundances

<table>
<thead>
<tr>
<th>Element</th>
<th>Number %</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>92.0</td>
<td>73.4</td>
</tr>
<tr>
<td>Helium</td>
<td>7.8</td>
<td>25.0</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.02</td>
<td>0.20</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.008</td>
<td>0.09</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.06</td>
<td>0.8</td>
</tr>
<tr>
<td>Neon</td>
<td>0.01</td>
<td>0.16</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.003</td>
<td>0.06</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.004</td>
<td>0.09</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.002</td>
<td>0.05</td>
</tr>
<tr>
<td>Iron</td>
<td>0.003</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Balmer H-gamma: \( n=3 \rightarrow n=2 \)
Emission Spectra and Flame Tests

Emission can only occur when electrons have been excited from their ground electronic configuration into higher energy levels. When these electrons return to a lower state, they emit photons of the same wavelength as those absorbed. (It’s the same energy difference, and the same effect as used to make AAS hollow cathode lamps.)

Atomic emission spectra are most commonly used as qualitative visual tests for the presence of an element in a sample, but they can be used quantitatively.

Flame Tests. An small sample is introduced into a flame. This excites a small fraction of electrons out of their ground state. Emissions in the visible range of wavelengths give the flame a characteristic colour. These wavelengths can be quantified by dispersion onto a detector.

The fraction of atoms excited in the flame is constant, and depends only on flame temperature. Hence the intensity of the emission is directly proportional to the number of atoms in the flame, and so can also be used to measure concentration in the aspirated sample.
Visible versus X-ray Spectrometry

Other atomic electron energy levels can be used to identify atoms:

Atomic spectrophotometry for identifying and measuring concentrations of elements suffers under some important practical constraints.

The visible and UV wavelength range corresponds to changes in outer electron configurations for most atoms. The energies involved are similar to or less than the ionization energy of the element. The samples to be analysed must therefore be decomposed into their constituent atoms. Sample preparation for AAS relies on breaking chemical bonds so that the electronic configurations are of atoms and not molecules.

X-rays probe much higher energy changes in core electron configurations. These are insensitive to bonding (which mainly effects outer shell electrons), so elaborate preparations are not required. Other restrictions arise when working with x-ray and higher energies.
Generation of X-rays

Electron Bombardment

X-rays are generated in a “cathode ray tube” by accelerating electrons from a cathode into a metal target anode. When the electrons strike the anode they collide and emit Bremsstrahlung or “braking” radiation in the x-ray wavelength range.

Braking may occur by one or more collisions, leading to a broad spectrum of emitted x-rays which have a well defined maximum energy (or minimum wavelength) corresponding to stopping by one collision.

\[ E_{\text{max}} = \frac{hc}{\lambda_{\text{min}}} \]
Worked Example: Bremsstrahlung Wavelengths

What is the minimum x-ray wavelength obtained when 30keV electrons impact on a Cu target?

The material used for the target is irrelevant to the bremsstrahlung minimum wavelength.

30keV electron have been accelerated by a 30,000V potential difference

\[ E = 30,000 \text{ eV} \times 1.609 \times 10^{-19} \text{ J/eV} = 4.83 \times 10^{-15} \text{ J} \]

The maximum x-ray energy or minimum wavelength correspond to complete stopping in one collision, i.e.

\[ \lambda_{\text{min}} = \frac{hc}{E_{\text{max}}} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{4.83 \times 10^{-15}} = 4.11 \times 10^{-11} \text{ m} \]

or 0.411 Å or 0.0411 nm.
X-ray wavelengths have been known for a long time, and are denoted by an older “shell” notation, K, L, M… corresponding to transitions into the $n = 1, 2, 3…$ levels. These spectra show the $K$ transitions.

X-Ray Fluorescence

In addition to the broad spectrum Bremsstrahlung, target anodes may exhibit sharp lines characteristic of the atom(s) in the anode. These spectra show the $K$ transitions. These arise when incident electrons have enough energy to ionise the atom by **ejecting an electron from a core** (e.g. 1s) **atomic orbital**.

X-ray photons are emitted when electrons drop from higher energy orbitals to fill the vacancy. Because these wavelengths are characteristic of core orbital energies, they are relatively unaffected by any changes in outer (valence) electron energies associated with bonding.

X-ray wavelengths are characteristic of the element being bombarded, and an x-ray fluorescence spectrum can be used to identify elements in a sample.
X-Ray Fluorescence - Minerals and Materials

The x-ray $K$ emissions arise from $2p \rightarrow 1s$ transitions, and these are enough to identify elements in minerals that cannot be vapourised. The energy of these transitions increases with $Z^2$ (as demonstrated by Moseley). For H this series is in the UV, and for heavier elements it moves into the x-ray range.

Core (1s) ionization that leads to x-ray fluorescence can be generated by UV excitation at low $Z$, electron or x-ray bombardment for intermediate $Z$, and $\gamma$-radiation for heavier elements.

Peak splitting is due to electron spin effects that we will not consider.
Astrochemistry - X-ray spectroscopy of the Universe

X-ray fluorescence is used to identify elements in stars, galaxies, and other features by their characteristic wavelengths. The supernova Tycho, observed in 1572, exhibits a broad x-ray spectrum as shown at right.

Resolving the x-ray spectrum into its characteristic wavelengths, it is possible to map the distribution of various elements around the supernova remnant. Some representative elements identified in this way are shown below.

- Calcium
- Sulphur
- Silicon
- Iron
Summary

You should now be able to

• Explain the difference between core and valence electrons.
• Distinguish between absorbance and emission spectra.
• Explain how AAS works
• Convert experimental data between transmission, absorbance, and concentration if given appropriate information.
• Calculate the minimum wavelength of bremsstrahlung radiation.
• Explain how the elements in stars and other celestial objects can be identified and their abundances measured from visible and x-ray spectrometry.

Next Lecture

• Properties of Materials