The Periodic Table

The position of an element in the Periodic Table indicates the arrangement of its valence electrons. For example, magnesium in the third period and second group has its valence electrons in the n = 3 shell and a total of two of them.

Valence Electrons are those in the outer most shell of an element and are responsible for the bonding characteristics of that element.

Core Electrons are the other electrons of an element and generally play no part in the reactivity and bonding of that element.

Periodic Trends

• First Ionisation Energy: $\mathsf{M} \, (\mathrm{g}) \rightarrow \mathsf{M}^+ \, (\mathrm{g}) + \mathrm{e}^-$

The first ionisation energy generally increases across a period and decreases down a group. This reflects the effective nuclear charge experienced by the electron being removed.

First E_i

The Atomic Radius is defined as half the distance between two atoms of the same element.

The slight drop in first ionisation energy from N to O results from an electron repulsion component as two electrons pair in a p orbital.

The atomic radius decreases across a period and increases down a group. This, once again, reflects the influence of effective nuclear charge.

Cations are always smaller, and anions larger, than the neutral atoms from which they are formed.

Question: Complete the following table:

Question: Predict the relative size of the elements: Cs, Be, Si, O, Te.

• Electronegativity is an empirical scale that represents the ability of an atom, when in a compound, to attract the electrons of a chemical bond towards itself.

Pauling assigned values to the elements on an arbitrary scale from 0 - 4. The trend shows an increase in electronegativity across a period and decreases down a group. Here, again, it is the influence of effective nuclear charge which underlies this trend.

Question: Why are there no values of electronegativity assigned to the Noble gases?

d-Block Elements (The Transition Metals)

Here the d-orbitals are being filled with electrons. Note that Cr and Cu have an 'unexpected' electron configuration, but understandable in terms of the additional stability a half filled or completely filled sub-shell possesses. In periods 5 and 6 the electron configuration of the transition metals appears more irregular and I do not expect you to predict them!

Trends in atomic radius, electronegativity and first ionisation energy are also observed among the transition metals but are not as clear as the trends in the main blocks of the Periodic Table.

and 5th Period are almost always found together in minerals and ores.

One of the most characteristic chemical properties of the d-block elements is the occurrence of multiple oxidation states. This allows for rich redox chemistry.

To determine the electron configuration of a (first row) transition metal ion, remove electrons from the 4s orbital before the 3d orbital.

Example: Write the electron configurations of the following atoms and ions.

Fe³⁺ [Ar] $3d^5$

Question: Write the electron configurations of the following atoms and ions.

Cr Cr^{2+} $Co³⁺$

 Zn^{2+}

Elements and the body

Percentage of atoms in the human body:

Example:

In a 75 kg adult, the typical mass of metals varies widely:

Metal ions in biology fall into three groups: groups:

1. Essential elements e.g. Na $^{\text{*}}$, K $^{\text{*}}$, Mg $^{2+}$, Ca²⁺, Fe^{2+/3+}, Cu^{+/2+} , $7n^{2+}$ $\frac{16}{8}$ 2. Toxic elements $\frac{63.55}{47}$
 $\frac{47}{107.67}$ e.g. Pb^{2+} , Hg²⁺, š $Be²⁺$ 3. Elements used in medicine e.g. Li⁺, Pt²⁺ essential toxic medicinal medicinal archaea

Biological Chemistry of Group 1 and Group 2 Ions

Where many transition metals are present at trace amounts in the body, the Group 1 and 2 ions, Na⁺, K⁺, Mg²⁺ and Ca²⁺ are present at, relatively, very high concentrations. Surprisingly Na⁺ performs very different roles to K⁺, and Mg²⁺ performs very different roles to Ca²⁺. Na⁺ and Ca²⁺ are concentrated in the body fluids outside the cells (extracellular) and K^* , Mg²⁺ are concentrated inside cells (intracellular). (The extracellular concentrations are of similar magnitude to those in seawater.) Maintaining a concentration gradient across a cell wall requires a pumping system, with the energy supplied by ATP. For instance, the Na⁺/K⁺-ATPase pump which acts like a 'revolving door' to transport ions across the cell membrane.

Sodium. Na⁺ is the principal extracellular solute and maintains the osmotic balance and tissue water content of the body. Cell membranes are permeable to water but not to inorganic solutes so water flows through the wall to balance the ionic strength. If this was not kept in balance the cells would dehydrate or explode.

. The Bottom is the inner membrane (inside of the Cell)

Some antibiotics work by binding ions such as Na⁺ and K⁺ and carrying them across the cell wall artificially altering ions concentrations and killing the cell. For example valinomycin has a hydrophilic interior that binds metal ions and lipophilic exterior that allows it to cross the cell wall.

Potassium. K⁺ is required for glucose metabolism, protein synthesis and activation of some enzymes (e.g. pyruvate kinase and dialkylglycine decarboxylase). The K^+ binds to anionic sites on the enzyme, changing its conformation and activating it.

Magnesium. Mg²⁺ has numerous roles but probably the most important is the $\text{Me}^{2+}/\text{ATP}^{4-}$ complex. The Mg^{2+} facilitates both the transport and hydrolysis of the ATP^{4-} ion, the species that is produced and used in greater amounts than any other compound on earth (250 million tonnes/day from people alone - 290 kg during this lecture!). ATP^{4-} is the main energy transport in the body. Mg²⁺ also transports other nucleotides and is involved in DNA/RNA synthesis (if Mg^{2+} is replaced by Mn²⁺ the rate of the reaction goes up dramatically but so does the error rate).

The interaction between Mg²⁺ and ATP⁴⁻

 Mg^{2+} has a high charge/radius ratio, which means it can also form strong bonds with N, e.g. in chlorophyll, the dominant light capturing molecule.

Calcium. Ca²⁺ fulfills a number of different roles including the control of many advanced biological systems, the stabilisation of polyanions such as DNA and in structural biominerals e.g. teeth and bones, apatite $Ca_{10}(PO_4)_6X_2$, where $X = F^-$, Cl^- or OH^- .

Biological Chemistry of Selected Transition Metals

Some transition metals are essential to the healthy functioning of the body. They are contained in the active sites of enzymes and proteins (called metalloproteins)

Transition metal elements are coordinated by metalloproteins because

- Many have a wide range of stable oxidation states, e.g. Mo(VI), Mo(V) and Mo(IV)
- The metals offer structural stability
- They may act as Lewis Acids

For example,

- Fe^{$2+/3+$}: electron transfer (cytochromes), oxygen carrying (hemoglobin)
- Cu^{+/2+}: electron transfer, catalysis (enzymes)
- Zn^{2+} : structural role, catalysis (enzymes)

Zinc has only one stable oxidation state $(2n^{2+})$ so is not used in electron transfer (redox) processes but in a structural role – where it binds to amino acids to fold them into a domain which is recognised by DNA – the 'zinc finger' proteins.

Toxic Metals

All elements are toxic if in high enough concentration (even Na⁺, K⁺)

Most transition metal elements are highly toxic and are very tightly controlled by the body. If these controls are defective, severe effects can result. E.g., Wilson's disease, a genetic abnormality that results if the body's ability to dispose of extra Cu²⁺ is impaired.

Other metals are quintessentially toxic, i.e., they have no known natural role in the body. The body can deal with some level of such elements but if these levels are exceeded, we need to use 'chelating ligands' to remove the excess element (chelation therapy). E.g. removal of Pb²⁺ using EDTA or removal of Cu^{2+} using penicillamine.

Medicinal Uses of Metals

Some metals are used as supplements (eg iron treatments for anaemia, calcium for osteoporosis) while other metals used for medicinal purposes have no natural role in the body.

E.g. Li⁺ used for the treatment of bipolar disease – probably interferes with the action of metals such as Mg²⁺ or Ca²⁺. Pt²⁺ used for the treatment of cancer – cis-[PtCl₂(NH₃)₂].