

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.

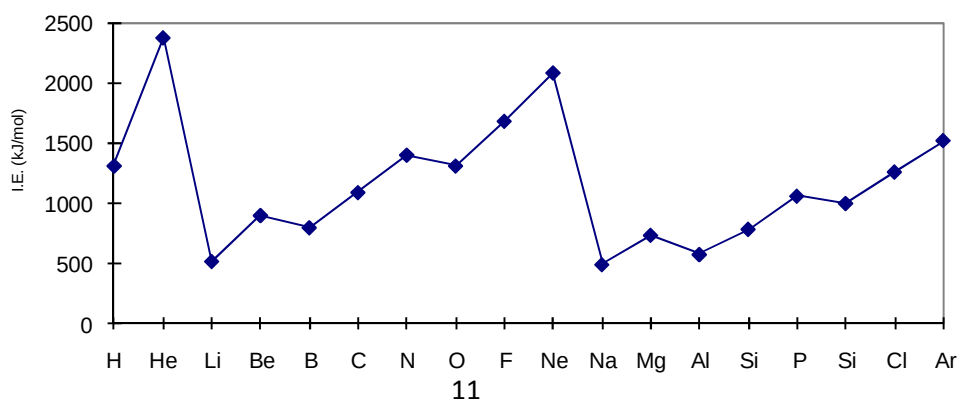
Core Electrons are the other electrons of an element and generally play no part in the reactivity and bonding of that element.

1	2											13	14	15	16	17	18
1 H 1.008												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
2 Li 6.941	3 Be 9.012											11 Na 22.99	12 Mg 24.31				
3 Na 22.99	4 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4 K 39.10	5 Ca 40.08	6 Sc 44.96	7 Ti 47.87	8 V 50.94	9 Cr 52.00	10 Mn 54.94	11 Fe 55.85	12 Co 58.93	13 Ni 58.69	14 Cu 63.55	15 Zn 65.41	16 Ga 69.72	17 Ge 72.64	18 As 74.92	19 Se 78.96	20 Br 79.90	21 Kr 83.80
5 Rb 85.47	6 Sr 87.62	7 Y 88.91	8 Zr 91.22	9 Nb 92.91	10 Mo 95.94	11 Tc (97.91)	12 Ru 101.1	13 Rh 102.9	14 Pd 106.4	15 Ag 107.9	16 Cd 112.4	17 In 114.8	18 Sn 118.7	19 Sb 121.8	20 Te 127.6	21 I 126.9	22 Xe 131.3
6 Cs 132.9	7 Ba 137.3	8 * 57-71	9 Hf 178.5	10 Ta 180.9	11 W 183.8	12 Re 186.2	13 Os 190.2	14 Ir 192.2	15 Pt 195.1	16 Au 197.0	17 Hg 200.6	18 Tl 204.4	19 Pb 207.2	20 Bi 209.0	21 Po (209.0)	22 At (210.0)	23 Rn (222.0)
7 Fr (223)	8 Ra (226)	9 ** 89-103	10 Rf (261)	11 Db (262)	12 Sg (266)	13 Bh (264)	14 Hs (277)	15 Mt (268)	16 Ds (271)	17 Rg (272)	18 Uub (285)	19 Uut (284)	20 Uuq (289)	21 Uup (288)	22 Uuh (292)		23 Uuo (294)

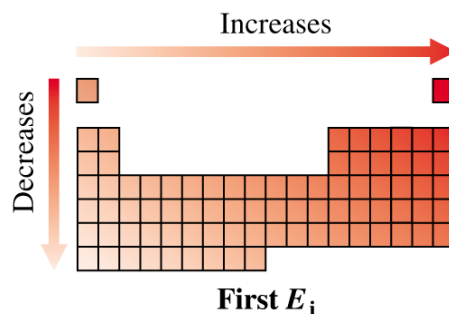
*lanthanide series	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
**actinide series	89 Ac (227)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Periodic Trends

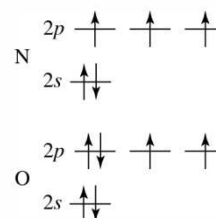
- First Ionisation Energy:** $M(g) \rightarrow M^+(g) + e^-$



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.

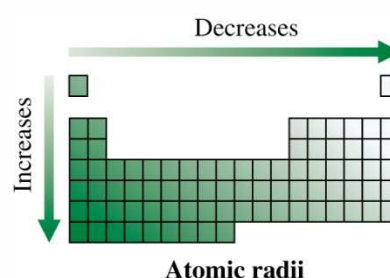


The slight drop in first ionisation energy from N to O results from an electron repulsion component as two electrons pair in a p orbital.



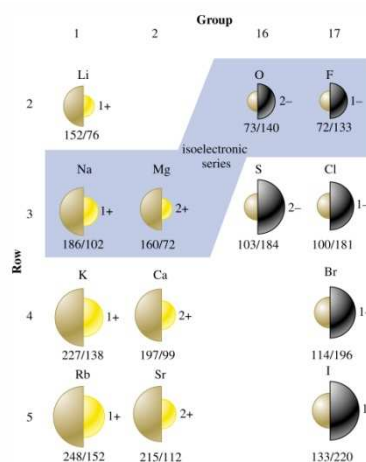
- **The Atomic Radius** is defined as half the distance between two atoms of the same element.

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.

Radius in nanometres:					
Li^+	0.060	C^{4+}	0.015		
Li	0.123	C	0.077	F	0.072
		C^{4-}	0.260	F^-	0.136

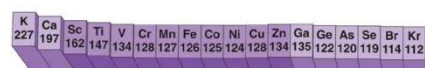


Question: Complete the following table:

Element	N^{3-}	O^{2-}	F^-	Ne	Na^+	Mg^{2+}	Al^{3+}
Atomic No							
No of electrons							
Relative size							

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

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.



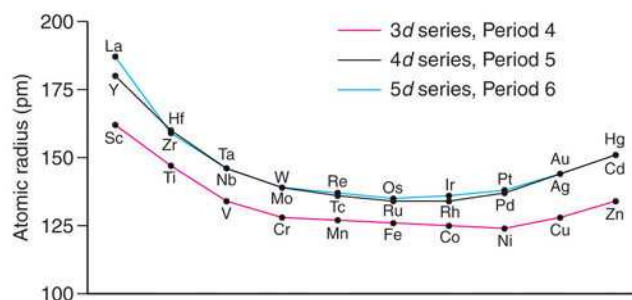
A Atomic radius (pm)



B Electronegativity



C First ionization energy (kJ/mol)



4d and 5d elements have very similar sizes due to the 'lanthanide contraction'. A consequence of this is that elements in the same Group of the 4th 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.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Group	3	4	5	6	7	8	9	10	11	12
Oxidation state	Valence configuration									
+1			d^4	d^5	d^6	d^7	d^8	d^9	d^{10}	
+2		d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
+3		d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	
+4		d^0	d^1	d^2	d^3	d^4	d^5	d^6		
+5			d^0	d^1	d^2	d^3	d^4			
+6				d^0	d^1	d^2				
+7					d^0					

■ = +2 ■ = +3, +4 ■ = d^0

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.



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

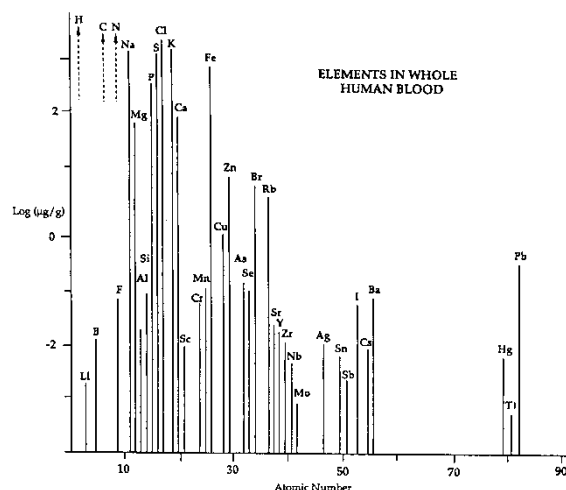


Elements and the body

Percentage of atoms in the human body:

Element	H	O	C	N	Others
%	62.8	25.4	9.4	1.4	1.0

Example:



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

Metal	Na	K	Ca	Mg	V	Cr	Mn	Fe	Co	Cu	Zn	Mo
Mass/g	70-120	160-200	1100	25	0.025	0.002	1	4-5	0.0012	0.08-0.12	2-3	0.010

Metal ions in biology fall into three groups:

- Essential elements
e.g. Na^+ , K^+ , Mg^{2+} , Ca^{2+} , $\text{Fe}^{2+/3+}$, $\text{Cu}^{+/2+}$, Zn^{2+}
- Toxic elements
e.g. Pb^{2+} , Hg^{2+} , Be^{2+}
- Elements used in medicine
e.g. Li^+ , Pt^{2+}

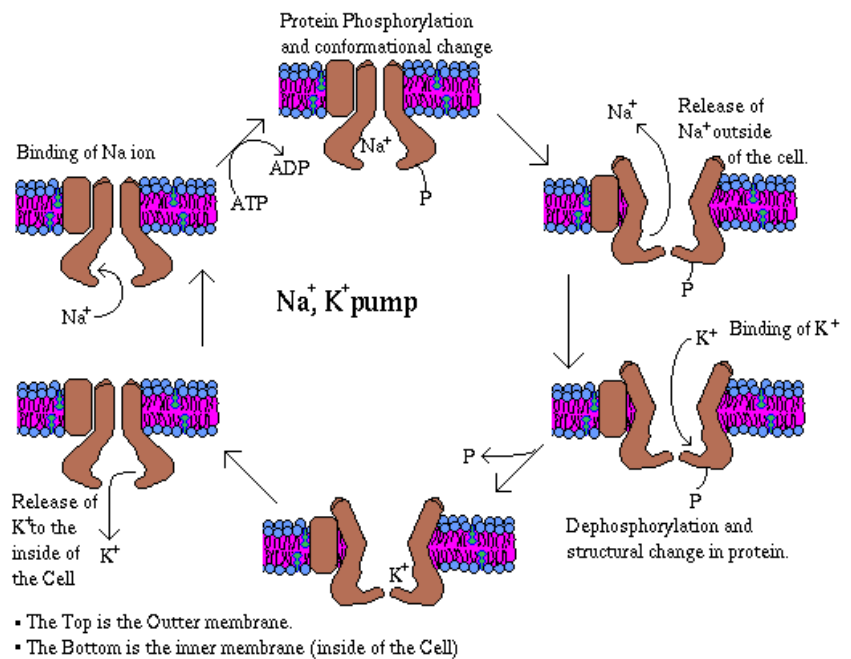
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55 Cs 132.91	56 Ba 137.34	57-71 Lanthanides	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
87 Fr [223]	88 Ra [226]	89-103 Actinides	104 Rf [261]	105 Db [262]	106 Sg [266]	107 Bh [264]	108 Hs [277]	109 Mt [268]	110 Ds [271]	111 Rg [272]	112 Cn [285]	113 Nh [286]	114 Fl [289]	115 Mc [290]	116 Lv [293]	117 Ts [294]	118 Og [294]
57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [144.91]	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97			
89 Ac [227.0]	90 Th 232.04	91 Pa [231.0]	92 U 238.03	93 Np [237.0]	94 Pu [239.1]	95 Am [243.1]	96 Cm [247.1]	97 Bk [247.1]	98 Cf [251.1]	99 Es [252.1]	100 Fm [257.1]	101 Md [258.1]	102 No [259.1]	103 Lr [260.1]			
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^+ , Mg^{2+} and Ca^{2+} are present at, relatively, very high concentrations. Surprisingly Na^+ performs very different roles to K^+ , and Mg^{2+} performs very different roles to Ca^{2+} . Na^+ and Ca^{2+} are concentrated in the body fluids outside the cells (extracellular) and K^+ , Mg^{2+} 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.

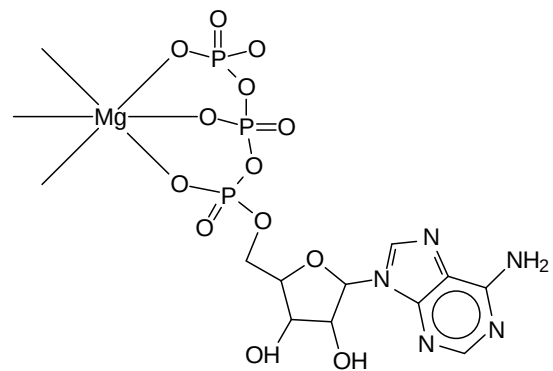
Sodium. Na^+ is the principal extracellular solute and maintains the osmotic balance and tissue water content of the body. Cell membranes are permeable to water but not to inorganic solutes so water flows through the wall to balance the ionic strength. If this was not kept in balance the cells would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



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. Mg^{2+} has numerous roles but probably the most important is the $\text{Mg}^{2+}/\text{ATP}^{4-}$ 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. Mg^{2+} also transports other nucleotides and is involved in DNA/RNA synthesis (if Mg^{2+} is replaced by Mn^{2+} the rate of the reaction goes up dramatically but so does the error rate).



The interaction between Mg^{2+} and ATP^{4-}

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. Ca^{2+} 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 $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$, where $\text{X} = \text{F}^-$, 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)

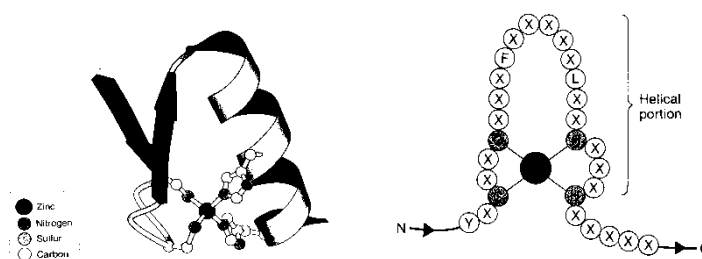
Transition metal elements are coordinated by metalloproteins because

- 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,

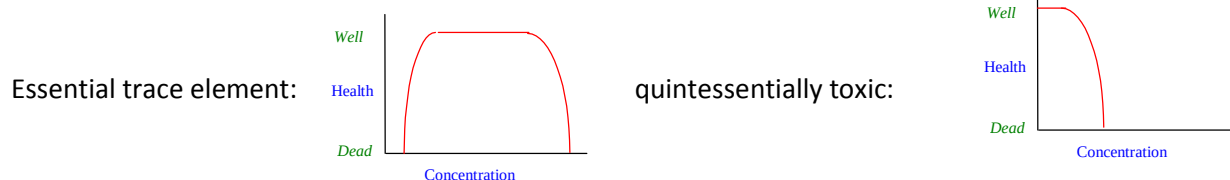
- $\text{Fe}^{2+/3+}$: electron transfer (cytochromes), oxygen carrying (hemoglobin)
- Cu^{+2+} : electron transfer, catalysis (enzymes)
- Zn^{2+} : structural role, catalysis (enzymes)

Zinc has only one stable oxidation state (Zn^{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 Cu^{2+} 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 Pb^{2+} 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 Mg^{2+} or Ca^{2+} . Pt^{2+} used for the treatment of cancer – *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$.