Mendeleev's Periodic Table of the Elements



Dmitri Mendeleev born 1834 in the Soviet Union.

In 1869 he organised the 63 known elements into a periodic table based on atomic masses. He predicted the existence and properties of unknown elements and pointed out accepted atomic weights that were in error.

Reihen	Grappe I. 	Groppe II.	Gruppe III. 	Gruppe 1V. RB ⁴ 80*	Gruppe V. All ² R ² O ⁵	Gruppe VI. RB ² BQ ³	Gruppe VII. AB B'0 ²	Groppe VIII.
1	H=1		0-0000000	17.1			· · · · ·	
2	Li = 7	Bc = 9,4	B=11	C=12	N=14	0=16	F = 19	
а	Na=23	Mg=24	A1=27,3	8i - 28	Pac 31	8-32	C1=35,5	1
4	K = 39	Cs = 40	-= 44	'Ti == 48	V == 51	Cr == 52	Mn=55	Fe=56, Co=59, Ni=59, Ca=63.
5	(Ca == 63)	Zn == 65	-=68	-= 72	A=75	Se = 78	Br == 80	
6	Rb == 85	Sr=87	?Yt= 58	Zr = 90	Nb == 94	96=0M	=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Se=118	81-122	Te=125	J=127	
8	Cs = 133	Ba = 137	7Di=138	7Co == 140	-	. –	-	
9	()	-	i –	-	_	_		
10	-	-	YEe = 178	7 La == 180	Ta = 182	W = 184	-	Os=195, Ir=197, It=198, Au=199.
11	(Au = 199)	Hg == 200	$T_{1} = 204$	Pb== 207	Bi = 208	-	-	
12	-	-		Th == 231	-	C=240	-	

T	b	e	1	1	e	II.

The periodic table is thus an arrangement of the elements in order of increasing atomic number.

Elements are arranged in rows called periods.

Elements with similar properties are placed in the same column. These columns are called groups.

The modern day periodic table can be further divided into blocks.

H	2											13	14	15	16	17	ł
Li	Be				d	bl	oc	k				в	C	N	0	F	
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	Р	S	Cl	
к	Ca	Sc	Ti	۷	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	>
Cs	Ba	La	Hf	Ta	w	Re	Os	Ir	Pt	Au	Hg	τι	Pb	Bi	Po	At	F
Fr	Ra	Ac	Unq	Unp	Unh		_	f	bl	oc	k						
Lan	thani	ides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	l
	ctini	des	Th	Pa	H	Nn	Pu	Am	Cm	Bk	Cf	Fs	Em	Md	No	11	Ē

http://www.chemsoc.org/viselements/pages/periodic_table.html

The s, p, d and f blocks

This course only deals with the s and p blocks.

The s block is concerned only with the filling of s orbitals and contains groups I and II which have recently been named 1 and 2.

The p block is concerned only with the filling of p orbitals and contains groups III to VIII which have recently been named 13 to 18.

Groups exist because the electronic configurations of the elements within each group are the same.

Group	Valence Electronic configuration
1	S ¹
2	s ²
13	s ² p ¹
14	s ² p ²
15	s ² p ³
16	s ² p ⁴
17	s ² p ⁵
18	s ² p ⁶

The type of chemistry exhibited by an element is reliant on the number of valence electrons, thus the chemistry displayed by elements within a given group is similar.

Physical properties

Elemental physical properties can also be related to electronic configuration as illustrated in the following four examples:

1. Ionisation energy

First ionisation energy

$$E(g) \longrightarrow E(g)^{+} + e^{-}$$

If the energy required to remove one electron from the gaseous elements is plotted against atomic number a definite periodic pattern appears.



1st ionisation energies:

- i) vary systematically
- ii) increase across a period
- iii) decrease down a group



Across each period there is a steady increase in nuclear charge.

This results in stronger Coulombic (electro-static) interaction between the most weakly bound electron and the nucleus and thus a general increase in ionisation energy.

Down each group the valence electrons are in progressively larger orbitals.



The valence electrons are thus further away from the nuclear charge. Also although nuclear charge increases down a group the core electrons shield the valence electrons. This results in lower ionisation energies.

But there are more subtle changes in ionisation energy.

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Close inspection shows that for:



The general increase across the period is not observed.

Electronic configurations must be considered.

Be $1s^22s^2$ B $1s^22s^22p^1$

Although boron has a higher nuclear charge (5 instead of 4) its first ionisation energy is lower because the outermost electron is in a 2p orbital which is bigger than the 2s orbital. Thus the electron is further from the nucleus.

The filled 2s orbital also shields the nuclear charge making the electron in the 2p orbital even easier to remove.

The overall effect is the slight reduction in first ionisation energy from Be to B. Identical arguments can be applied for Mg to Al only now the 3s and 3p orbitals are involved. An Introduction to General / Inorganic Chemistry

Now consider N to O:



In oxygen two electrons now fill one p-orbital. The most weakly bound electron in oxygen is the same distance from the nucleus as it is in nitrogen as both electrons are in a 2p orbital. However, in oxygen the paired electrons interact via Coulombic repulsion which results in a reduction in the ionisation energy

2. Electron Affinity

Elements on the right hand side of the periodic table readily accept electrons, particularly the halogens of group VII / 17.

Fluorine, Chlorine, Bromine, Iodine, Astatine

 $X(g) + e^{-} \longrightarrow X^{-}(g)$

The addition of one electron leads to a more stable electronic configuration, *i.e.* that of the nearest noble gas. The electron affinity of the elements does not lend itself to a discussion of periodic trends.

3. Electronegativity

However, the ability of nuclei to attract electrons leads to a very important concept, namely electronegativity.

This is the tendency of atoms involved in covalent bonds to attract electrons towards themselves.

An atom which tends to attract electrons is said to be electronegative.

An atom which tends to repel electrons is said to be electropositive.

Electronegativity is affected by:

- 1) atomic radius
- 2) nuclear charge
- 3) shielding by lower orbitals

In a manner similar to ionisation energies, the electronegativities of the elements also show periodic behaviour.



Electronegativities tend to:

- 1. increase along a period
- 2. decrease down a group

Electronegativities determine the covalent / ionic nature of bonds and thus the type of reactivity of molecules.

Electronegativities are quoted using an empirical scale named after Linus Pauling:





Linus Pauling born 1901 in Portland, USA.

Awarded Nobel prize for Chemistry in 1956 for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances.

The greater the difference between the electronegativities of two elements in a bond, the more ionic character the bond will have.

e.g. LiF will have more ionic character than AICI3.

The same logic can also be applied to predicting reactivity of covalent compounds. Symmetrical molecules such as O_2 and N_2 have no electronegativity difference between the atoms – thus no bond polarity. However, most chemical

bonds are asymmetric. The result is polar bonds as the more electronegative atom attracts the electrons towards it.





4. Atomic Radius

Atomic radii decrease across a period.

e.g. the radius of a sodium atom is 157 pm whilst that of a chlorine is 99 pm.



Six electrons, six protons and a number of neutrons have been added - how can the atom be smaller?

Both the neutrons and protons are added to the nucleus which is of negligible size. The electrons are added to the same 3s and 3p orbitals – thus there is no orbital size increase. However, the increased nuclear charge attracts the electrons to the nucleus more strongly resulting in the observed decrease in atomic radius.

Atomic radii increase down a group.

Although nuclear charge increases, the larger, outermost orbitals are screened by the inner core electrons.

What about the radii of ions compared to atoms?

Cations have smaller radii than atoms due to increased electron attraction to the nucleus.

Na 157 pm Na^+ 98 pm

Anions have larger radii than atoms due to increased electron repulsion and decreased electron attraction to the nucleus.

F 64 pm F⁻ 133 pm

Isotopes and Radioactivity

The periodic table comprises elements. Type of elemental is determined by number of protons, termed the atomic number (Z).

It is possible for atoms of the same element to have different numbers of neutrons and hence different mass numbers.

Such species are called isotopes.

Isotopes of a given element have:

- 1) identical electronic structures
- 2) identical chemical properties
- 3) different physical properties
- 4) different abundancies

All elements have isotopes. In all but one case isotopes have the same elemental symbol: *e.g.*



However there is one special case - the isotopes of hydrogen:

Isotopes of Hydrogen



Here each isotope has its own name:

¹ H	_	hydrogen
D	—	deuterium
³ T		tritium

The deuterium analogue of water – D_2O is the substance known as heavy water. It is about 10% heavier than ordinary water.



Mass Spectrometry

How do we determine the abundance of isotopes?

This is achieved using a technique called mass spectrometry.

A technique for measuring the mass to charge ratio of positive ions.



The greater the mass to charge ratio, the greater the magnetic field that must be applied for the ion to reach the detector.

Thus isotopes can be separated by altering the magnetic field.

This yields information on relative abundance of isotopes. e.g. chlorine exists as two isotopes ³⁵Cl and ³⁷Cl in a 3:1 ratio.



Of course, mass spectra of molecules are often more complicated. e.g. 2-methylpentane.



Relative Atomic Mass (RAM)

Relative Atomic Mass of an element is the weighted mean of isotopic masses of the naturally occurring isotopes of that element.

i.e. it accounts for the relative abundance of each isotope.

It is based on a scale which takes ${}_{6}^{12}C$ as the standard having a mass of 12.000 amu.

RAM = 12 x mass of 1 atom of the element

mass of 1 atom of ¹²C

How do we calculate relative atomic masses of the elements?

Isotope	Isotopic Mass	% Abundance
³⁵ Cl	34.969 amu	75.4
³⁷ CI	36.966 amu	24.6

The contribution of each respective isotope is given by:

isotopic mass x % natural abundance

³⁵ Cl contributes	34.969 x 75.4/100 =	26.366
³⁷ CI contributes	$36.966 \times 24.6/100 =$	9.094
RAM of chlorine	= 26.366 + 9.094	
	=	35.460

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Radioactivity concerns the spontaneous disintegration of the nucleus of an unstable atom.

Unstable isotopes of elements are referred to as radionuclides. The disintegration occurs in one of three ways, each emitting a kind of radiation:

 α alpha, β beta and γ gamma

Each of these radiations is affected differently by electric fields. Alpha radiation is drawn to the cathode, beta radiation to the anode and gamma radiation is unaffected.

α -Radiation

Comprises α -particles which are high velocity ${}_{2}^{4}He$ nuclei - in effect He²⁺ ions. Generally emitted by heavy nuclei with atomic number > 83. α -particles have very high kinetic energy due to their high mass and are very ionising.

They have a range of 1-8 cm in air.

 α -emission $^{238}_{92}U \rightarrow ^{234}_{90}Th + ^{4}_{2}He$

β-Radiation

Comprises extremely fast moving electrons from 3-99% of the speed of light - referred to as β -particles. They result from the transmutation of neutrons

$$^{1}_{0}n \rightarrow ^{1}_{1}p + ^{0}_{-1}e + v$$

The mass and energy changes for this process are balanced by the emission of an anti-neutrino (v) (*i.e.* an anti-matter particle with negative mass!)

 β -particles have a range of 1-2 m in air and can pass through up to 3 mm of solid lead.

 β -emission ${}^{234}_{90}$ Th $\rightarrow {}^{234}_{91}$ Pa $+ {}^{0}_{-1}$ e