

Semester-4 (C9/T9)

Department of Chemistry
Panchmura Mahavidyalaya

s–block Group 1

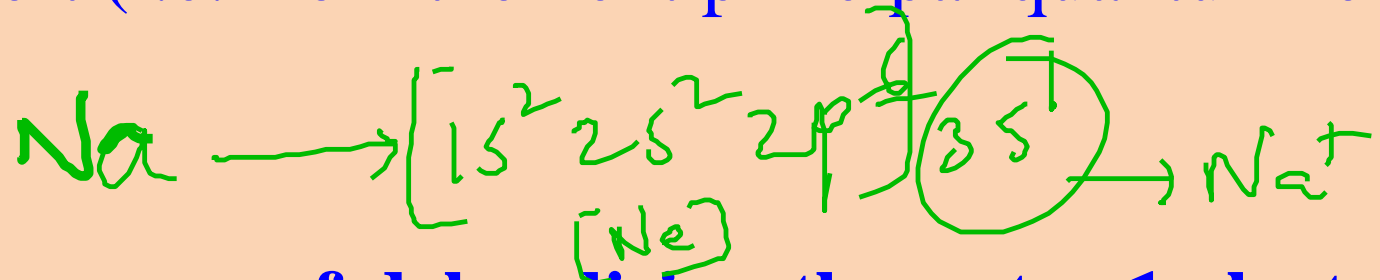
(Alkali Metals)

Introduction to the s block elements - Group 1 Alkali Metals

Pd	s block elements		d blocks and f blocks of metallic elements										p block elements					
	Gp1	Gp2											Gp3/ 13	Gp4/ 14	Gp5/ 15	Gp6/ 16	Gp7/ 17	Gp0/ 18
1	${}_1\text{H}$																	${}_2\text{He}$
2	${}_3\text{Li}$ lithium	${}_4\text{Be}$ beryllium	The modern Periodic Table of Elements ${}_z\text{Symbol}$, z = atomic or proton number										${}_5\text{B}$	${}_6\text{C}$	${}_7\text{N}$	${}_8\text{O}$	${}_9\text{F}$	${}_{10}\text{Ne}$
3	${}_{11}\text{Na}$ sodium	${}_{12}\text{Mg}$ magnesium	highlighting position of Group 1 and Group 2 elements										${}_{13}\text{Al}$	${}_{14}\text{Si}$	${}_{15}\text{P}$	${}_{16}\text{S}$	${}_{17}\text{Cl}$	${}_{18}\text{Ar}$
4	${}_{19}\text{K}$ potassium	${}_{20}\text{Ca}$ calcium	${}_{21}\text{Sc}$	${}_{22}\text{Ti}$	${}_{23}\text{V}$	${}_{24}\text{Cr}$	${}_{25}\text{Mn}$	${}_{26}\text{Fe}$	${}_{27}\text{Co}$	${}_{28}\text{Ni}$	${}_{29}\text{Cu}$	${}_{30}\text{Zn}$	${}_{31}\text{Ga}$	${}_{32}\text{Ge}$	${}_{33}\text{As}$	${}_{34}\text{Se}$	${}_{35}\text{Br}$	${}_{36}\text{Kr}$
5	${}_{37}\text{Rb}$ rubidium	${}_{38}\text{Sr}$ strontium	${}_{39}\text{Y}$	${}_{40}\text{Zr}$	${}_{41}\text{Nb}$	${}_{42}\text{Mo}$	${}_{43}\text{Tc}$	${}_{44}\text{Ru}$	${}_{45}\text{Rh}$	${}_{46}\text{Pd}$	${}_{47}\text{Ag}$	${}_{48}\text{Cd}$	${}_{49}\text{In}$	${}_{50}\text{Sn}$	${}_{51}\text{Sb}$	${}_{52}\text{Te}$	${}_{53}\text{I}$	${}_{54}\text{Xe}$
6	${}_{55}\text{Cs}$ cesium	${}_{56}\text{Ba}$ barium	57-71	${}_{72}\text{Hf}$	${}_{73}\text{Ta}$	${}_{74}\text{W}$	${}_{75}\text{Re}$	${}_{76}\text{Os}$	${}_{77}\text{Ir}$	${}_{78}\text{Pt}$	${}_{79}\text{Au}$	${}_{80}\text{Hg}$	${}_{81}\text{Tl}$	${}_{82}\text{Pb}$	${}_{83}\text{Bi}$	${}_{84}\text{Po}$	${}_{85}\text{At}$	${}_{86}\text{Rn}$
7	${}_{87}\text{Fr}$ francium	${}_{88}\text{Ra}$ radium	89-103	${}_{104}\text{Rf}$	${}_{105}\text{Db}$	${}_{106}\text{Sg}$	${}_{107}\text{Bh}$	${}_{108}\text{Hs}$	${}_{109}\text{Mt}$	${}_{110}\text{Ds}$	${}_{111}\text{Rg}$	${}_{112}\text{Cn}$	${}_{113}\text{Uut}$	${}_{114}\text{Fl}$	${}_{115}\text{Uup}$	${}_{116}\text{Lv}$	${}_{117}\text{Uus}$	${}_{118}\text{Uuo}$

- ❖ outer electrons: Group 1 ns^1
- ❖ The first two vertical columns of the Periodic Table, i.e. Groups 1 and 2, are called the s-block metals, because they only have 1 or 2 electrons in their outer shell.
- ❖ These outer electrons are of an s-orbital type (s sub-shell or sub-quantum level) and the chemistry of the metals, with their relatively low ionisation energies, is dominated by the loss of these s electrons to form a cation and also accounts for their generally high chemical reactivity ...
- ❖ the **outer s^1 electron** loss by the Group 1 Alkali Metals gives the M^+ ion,
- ❖ and in each case the cation has a residual very stable noble gas core of electrons.

- ❖ **The only chemically stable oxidation states are +1 for Group 1 metals**, governed by the relative ease of loss of the outer s electrons and the subsequent very high ionisation energies required to remove a 2nd (for group 1) electron from the inner noble gas core of electrons left (i.e. from the next principal quantum level or shell).



- ❖ **The relative ease of delocalising the outer 1 electron in the metal lattice makes them good conductors of heat and electricity .**

lattice | Packing

- ❖ The low ionisation energies and low electronegativity means that when combined with non-metals, most compounds of the Group 1 elements tend to be ionic in nature.
- ❖ Group 1 ions and their compounds are important in the natural world of living systems and geology.
- ❖ Sodium and potassium ions (Na^+ and K^+) are important components of a balanced electrolyte solutions in living systems and in nerve impulse transmission systems.

Information and Data Table

GROUP 1 ALKALI METALS (from left to right is down the group!)

property \ Z symbol, name	₃ Li Lithium	₁₁ Na Sodium	₁₉ K Potassium	₃₇ Rb Rubidium	₅₅ Cs Caesium	₈₇ Fr Francium
melting point/°C	181	98	64	39	29	27
boiling point/°C	1347	883	774	688	679	677
density/gcm ⁻³	0.53	0.97	0.86	1.48	1.87	>1.87
1st IE/kJmol ⁻¹	513	496	419	403	376	400
2nd IE/kJmol ⁻¹	7298	4562	3051	2632	2420	2100
atomic metallic radius/pm	152	186	231	244	262	270
M ⁺ ionic radius/pm	78	98	133	149	165	180
electronegativity	0.98	0.93	0.82	0.82	0.79	0.70
electron configuration	2,1	2,8,1	2,8,8,1	2,8,18,8,1	2,8,18,18,8,1	2,8,18,32,18,8,1
electron configuration	[He]2s ¹	[Ne]3s ¹	[Ar]4s ¹	[Kr]5s ¹	[Xe]6s ¹	[Rn]7s ¹
Electrode potential M/M ⁺	-3.04V	-2.71V	-2.92V	-2.92V	-2.92V	-2.92V
Symbol – flame colour	Li – red/crimson	Na – yellow	K – lilac/purple	Rb – red	Cs – blue	Fr – na

outer electrons: Group 1 ns¹ and Group 2 ns²

- ❖ **Typical metals in some ways** e.g. silvery grey lustrous solids*, very good conductors of heat and electricity, relatively high boiling points.
 - ❖* When freshly cut they are quite shiny, but they rapidly tarnish by reaction with oxygen to form an oxide layer, which is why they are stored under oil.
 - ❖ The 1st ionisation energies are the lowest of any group of elements, but note the jump up to a very high 2nd ionisation energy.
 - ❖ Equations for the 1st and 2nd ionization energies.
 - $M(g) \implies M^+(g) + e^-$ (very low 1st IE, $M = \text{Li, Na, K, Rb, Cs, Fr}$)
 - $M^+(g) \implies M^{2+}(g) + e^-$ (much higher 2nd IE)
 - The very high 2nd ionization energy is due to removing an electron from an electronically very stable noble gas inner core of electrons.

- ❖ Untypical in other ways e.g. relatively soft, low density (Li, Na and K float on water before reacting ...), and very low melting points.
 - The reasons for the low melting points, densities and physical hardness lies in looking at the bonding model for metals.
- ❖ The more electrons that can be delocalised and the closer the atoms (actually ions in a metallic lattice) can approach each other the stronger the bond, thereby raising melting points, densities and tensile strength.
- ❖ However, Group 1 metals can only release one electron per atom to contribute towards the pool of bonding delocalised electrons. Also, being the first element on a given period, they have the highest relative atomic/ionic radii because you have the minimum nuclear attractive force on the outer electrons.

- **Any metal flame colour is due to electronic transitions in the atom or cation.**

❖ Electrons are promoted to higher quantum levels via collisions of the high thermal kinetic energy particles in the hot flame. When the promoted electron 'relaxes' or 'falls' back to its more stable electronic level, energy is emitted (this is the basis of an emission spectrum). If the frequency/wavelength/energy of the photons emitted is in the visible region of the electromagnetic spectrum, a 'flame colour' results e.g. as observed in fireworks.

- ❖ The set of quantum levels and associated energies are unique for each atom which means the quantum level differences varies from atom to atom, therefore the frequency/energy of emitted photons is different, hence you see different flame colours in the visible region of light from Group 1 metal – each element has a 'finger print' emission spectrum.
- ❖ The s–block groups 1/2 have the lowest ionisation energies of all the elements in the periodic table, so the high temperature of the flame ($>1000^{\circ}\text{C}$) means that the kinetic energy of the flame particles is quite sufficient to promote electrons to a higher quantum level when the metal atoms collide with other high KE atoms or molecules.

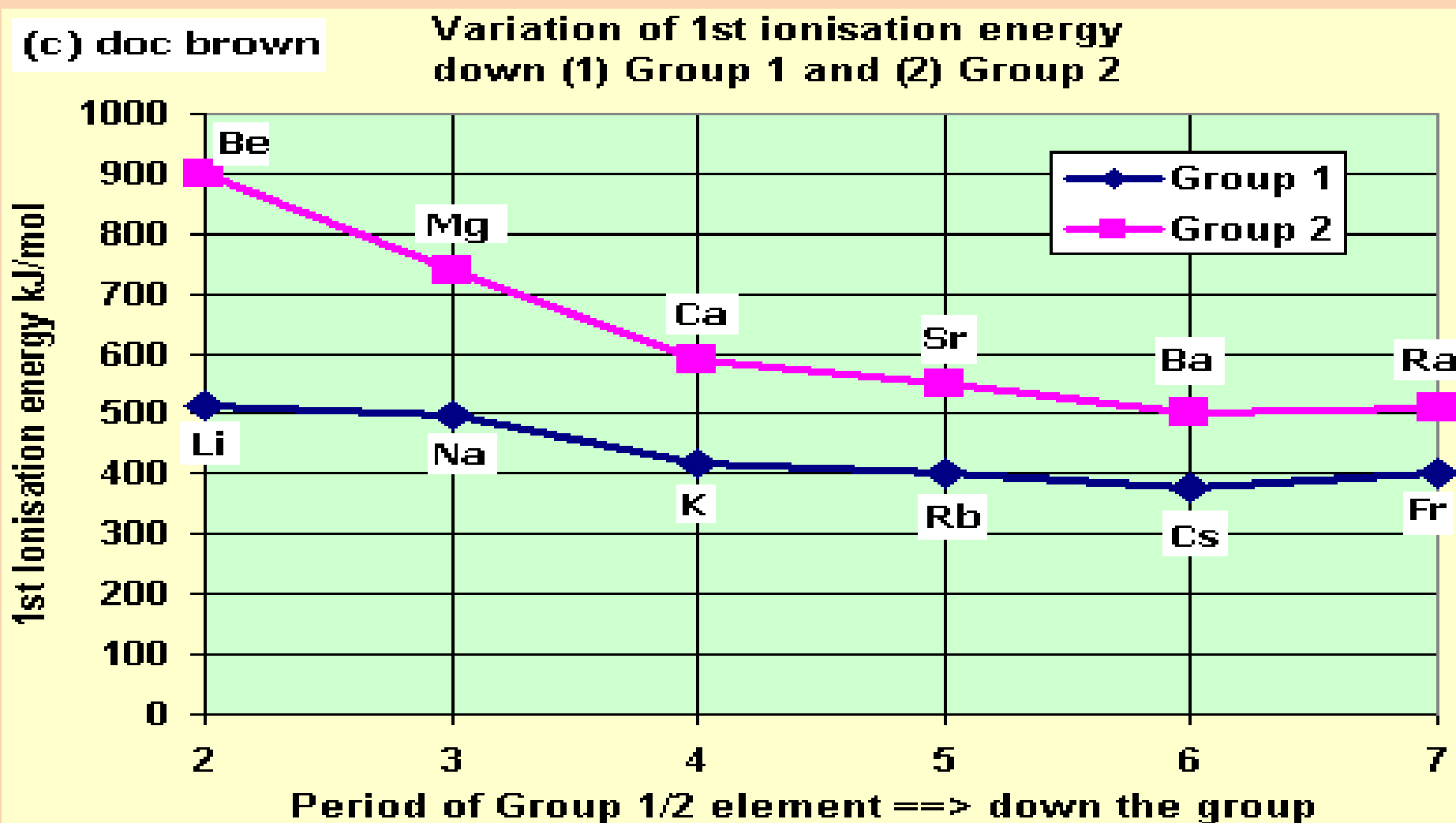
- ❖ Planck's Equation: $\Delta E = h\nu$, where
- ❖ $\Delta E = E_2 - E_1$, the energy difference between e.g. the outer s level E_1 and a higher level E_2 ,
- ❖ h = Planck's constant and ν = frequency of light of the emitted photons.
- ❖ **Oxidation state or oxidation number is always +1 in Group 1 Alkali Metal compounds.**
 - ❖ **Only** the single outer s–electron is easily lost, the 2nd, and subsequent ionisation energies are far too high to form chemically stable cations of 2+ etc. i.e. the energy required will not be compensated by ionic bond formation.
 - ❖ The stable Group 1 cation has the electron configuration of a noble gas,
 - e.g. the sodium atom, **Na**, is **2,8,1** or **$1s^2 2s^2 2p^6 3s^1$** or **[Ne]3s¹**
 - so the sodium ion, **Na⁺**, is **2,8** or **$1s^2 2s^2 2p^6$** or **[Ne]**



- **NOTE that Francium is highly radioactive and therefore difficult and dangerous to study BUT all its known physical and chemical properties fit in with it being at the foot of Group 1 and other properties could be inferred from the properties and group trends of Li to Cs.**

General Trends down groups 1 & 2 with increasing atomic number and formula patterns

The 1st ionisation energy (IE) or 2nd etc. decrease:



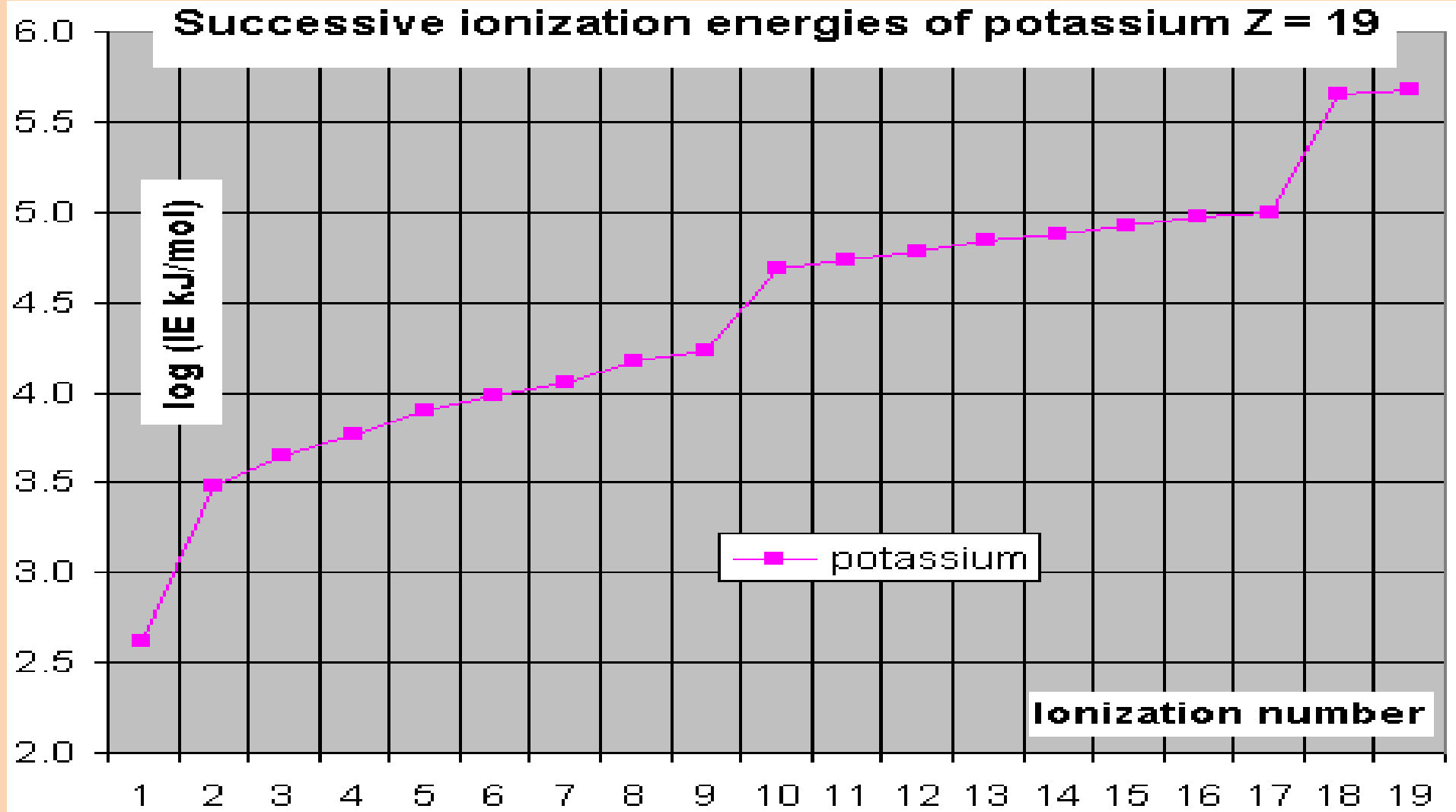
- ❖ because as you go down the group from one element down to the next, on the next period, the atomic radius gets bigger due to an extra filled electron shell.
- ❖ The outer electrons are further and further from the nucleus and are also shielded by the extra full electron shell of negative charge. Therefore the outer electrons are less and less strongly held by the positive nucleus and so less and less energy is needed to remove them.

- ❖ Despite the significant increase in atomic number i.e. positive nuclear charge down the group, this effect is outweighed by 'shielding effects' of inner full electron shells and also the nuclear charge is spread over an increasingly larger surface as the atomic radius increases.
- ❖ The effective nuclear charge is NOT what it seems as given by the atomic number and is more related to the number of outer electrons and the size of the atom.

IONISATION

ENERGY

PATTERNS



Successive ionisation energies always increase

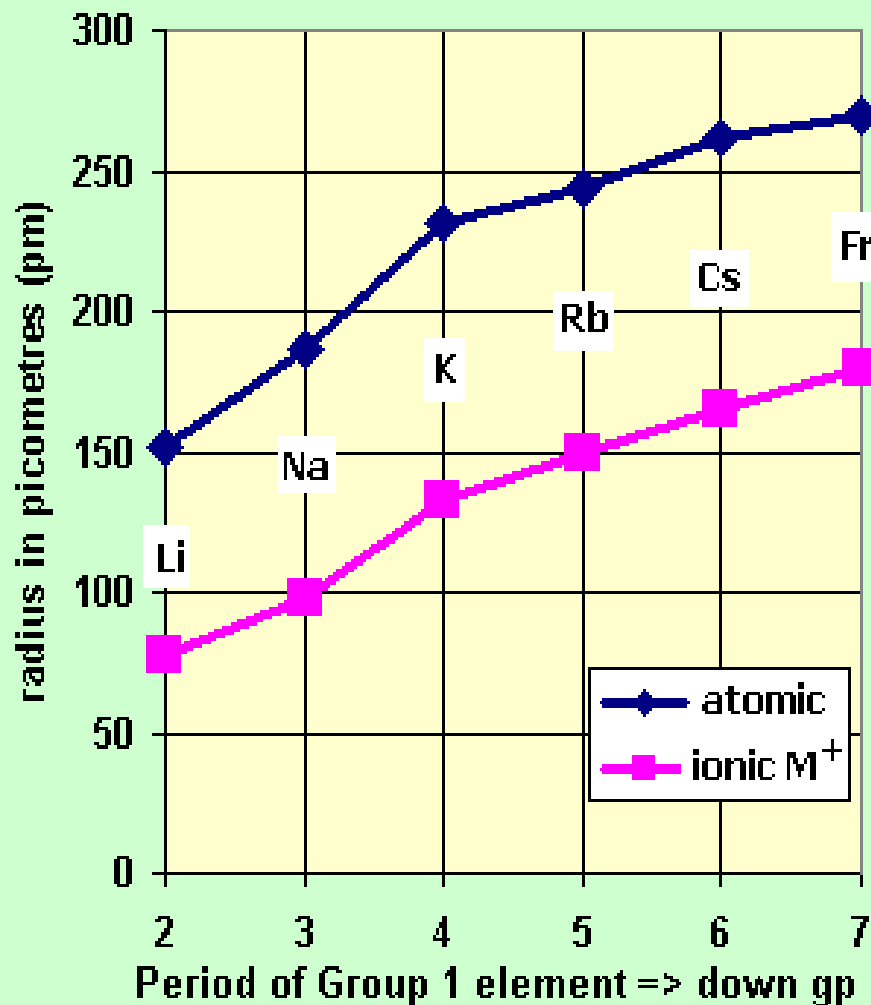
e.g. ... 3rd > 2nd > 1st ...

- ❖ because the same nuclear charge is attracting fewer electrons and on average closer to the nucleus.
- ❖ The negative electrons are being successively removed from an increasingly more positive ion, so, not surprisingly, more energy is required.
- ❖ BUT note the 2nd IE for Group 1 (e.g. for potassium in the right graph above), show a particularly significant increase in IE compared to the previous ionisation energy or energies.

- ❖ This is due to removing an electron from an electronically highly stable full inner shell and puts an upper limit on the chemically stable oxidation state.
- ❖ These abrupt changes in the successive ionisation energy graphs are clear evidence of principal quantum levels that the electrons occupy.

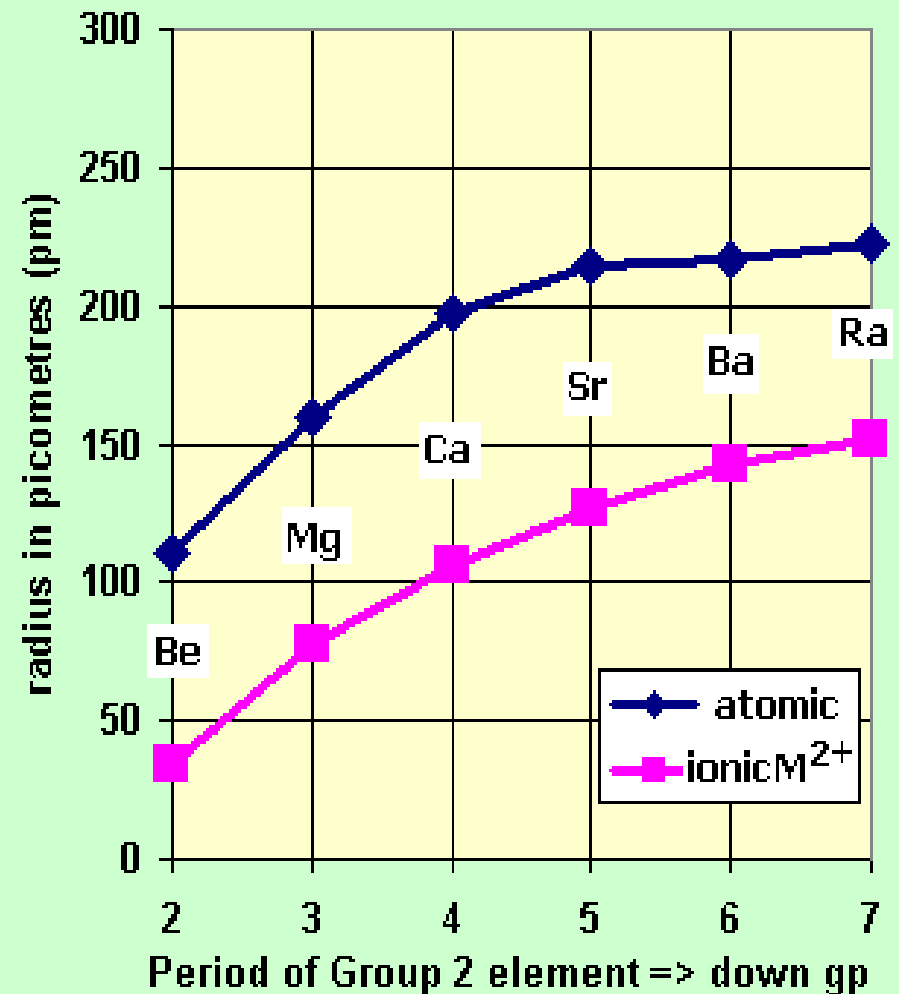
Atomic and ionic radius increases:

Variation of (1) atomic radius and (2) ionic radius down Group 1



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Variation of (1) atomic radius and (2) ionic radius down Group 2



- ❖ Because from one element to the next, an extra shell of electrons is added, increasing the electron 'bulk' and the outer electrons are increasingly less strongly held (see above).
- ❖ The radii of the adjacent Grp 2 atom is smaller than Gp 1 atom on the same period, because the nuclear charge has increased by one unit (L to R in PT), but is attracting electrons in the same shell.

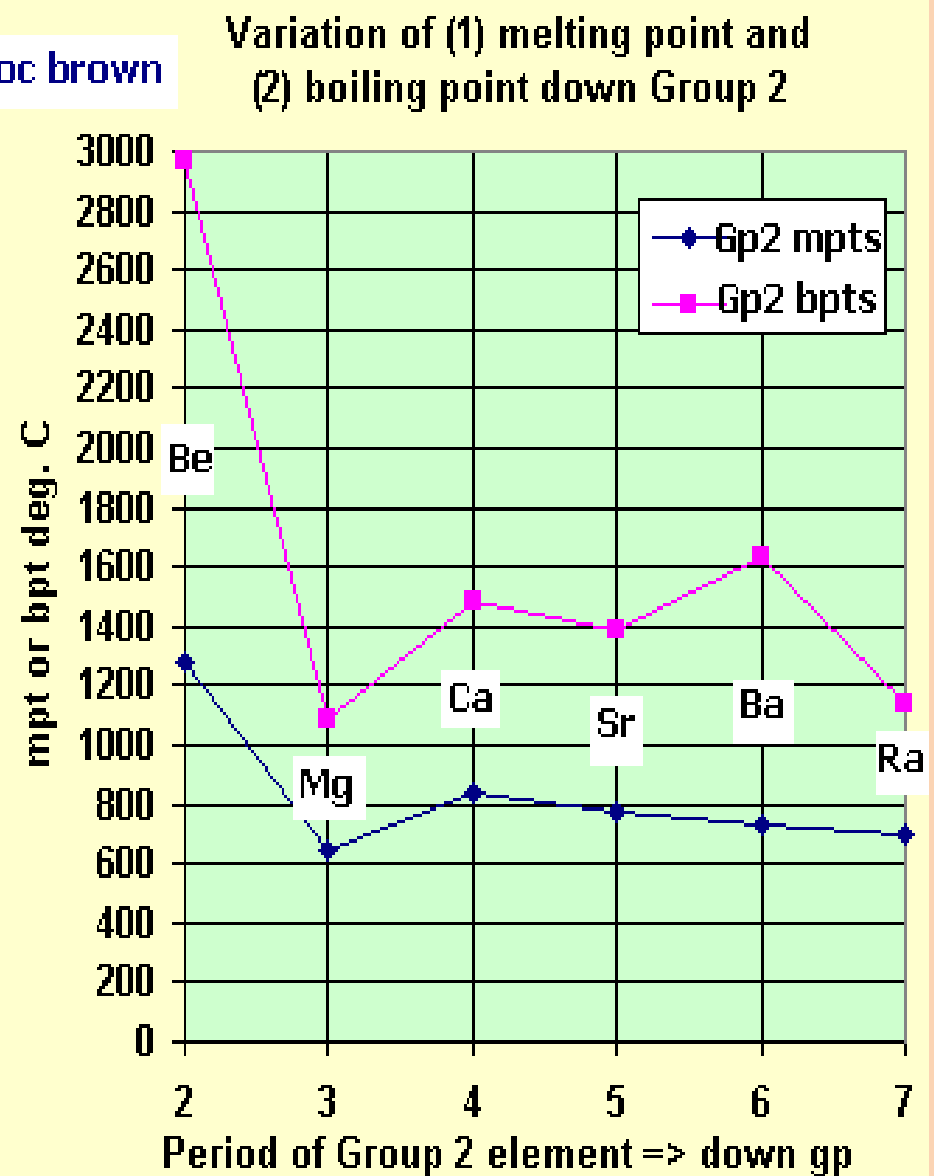
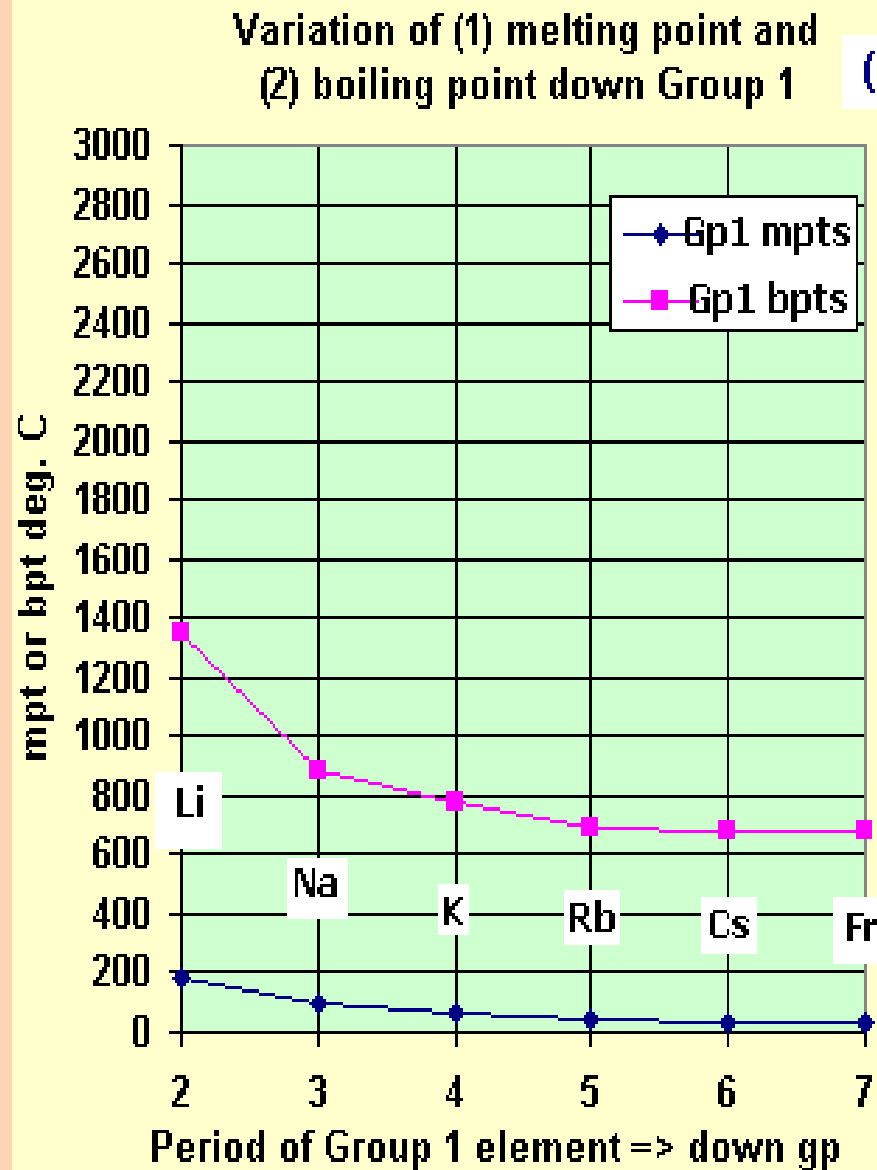
REACTIVITY TREND THEORY – relate to atomic radius and ionisation energy

- ❖ The metal gets more reactive down the group because ...
- ❖ When an alkali metal atom reacts, it loses an electron to form a singly positively charged ion e.g. $\text{Na} \implies \text{Na}^+ + \text{e}^-$ (in terms of electrons 2.8.1 \implies 2.8 and so forming a stable ion with a noble gas electron arrangement).
- ❖ As you go down the group from one element down to the next the atomic radius gets bigger due to an extra filled electron shell.

- ❖ The outer electron is further and further from the nucleus and is also shielded by the extra full electron shell of negative charge.
- ❖ Therefore the outer electron is less and less strongly held by the positive nucleus.
- ❖ This combination of factors means the outer electron is more easily lost, the M^+ ion more easily formed, and so the element is more reactive as you go down the group – (best seen in the laboratory with their reaction with water).
- ❖ The reactivity argument mainly comes down to increasingly lower ionisation energy down the group.
- ❖ The reaction of a group 1 metal with oxygen, water or halogens gets more vigorous as you descend the group.

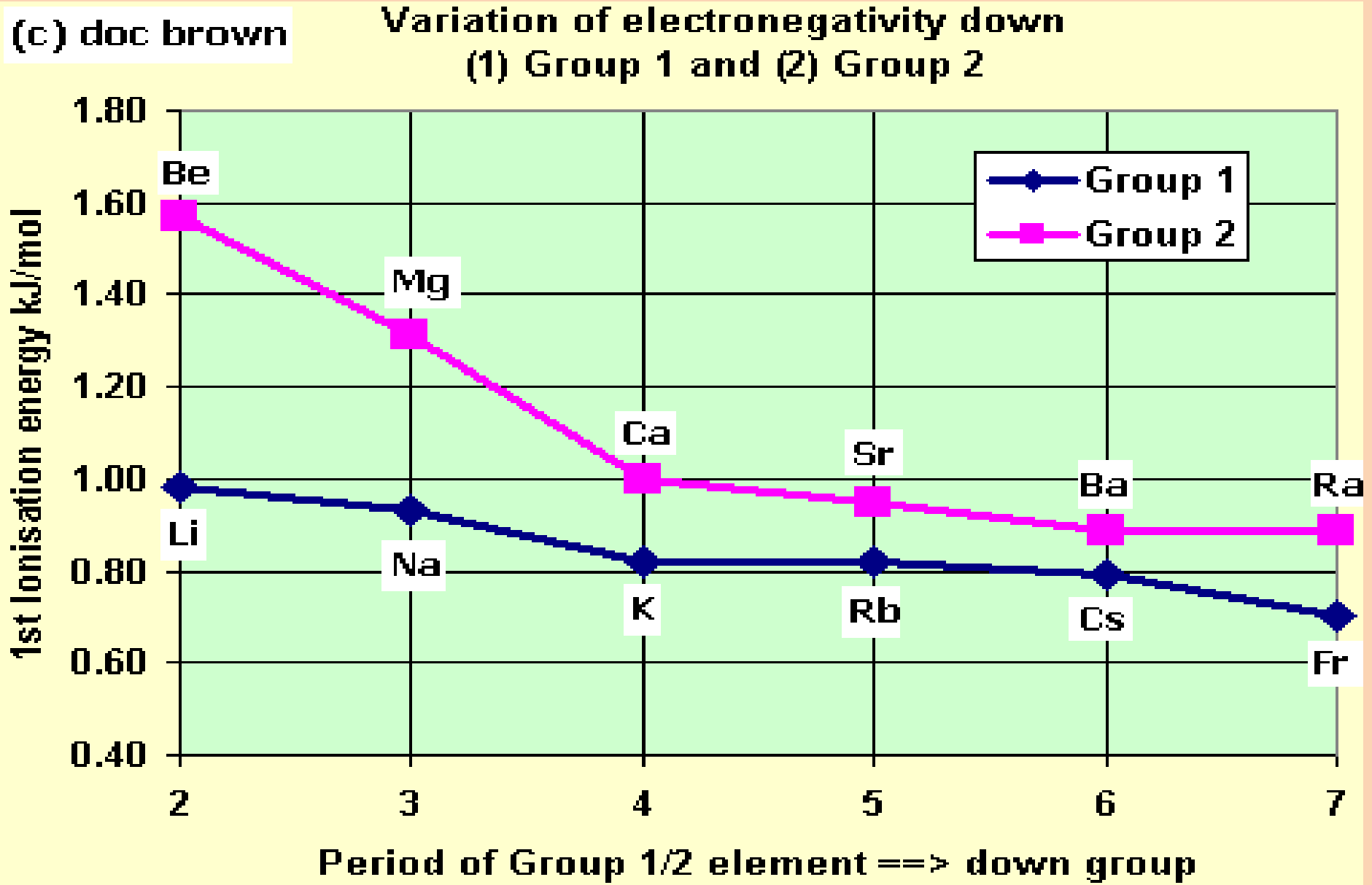
Generally (but not always), the melting and boiling points fall steadily:

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- ❖ This is because the ionic radii increase down the group increasing charge separation between the metal cations of the lattice and the free delocalised electrons.
- ❖ This weakens the electrical attractive bonding force and so less thermal KE is needed to weaken the lattice to the 'collapse point' i.e. melting.
- ❖ BUT the situation is not as simple as might be expected, e.g. the metal ions do not always have the same crystal lattice packing arrangement.

The electronegativity tends to decrease:



- ❖ The electronegativity values are the lowest of the elements, but there is still a group trend.
- ❖ They get lower because the effective nuclear attractive force on the outer electron charge decreases down the group.
- ❖ **You can explain it along the lines of the decreasing 1st IE argument (above), by merely changing the last part of the argument from 'easier to lose electron' to 'weaker attraction of electron charge'.**

Formula patterns:

- ❖ The general formulae are written in the summary tables in two ways
- ❖ 'simple' format M_2O or ionic formulae $(M^+)_2O^{2-}$ where M represents Li to Fr
- ❖ Since all compounds can be considered ionic, most formulae needed are readily derived in principle by knowing the formula and charge of 10 ions!
- ❖ All formulae are readily derived from equating the total positive charge of the cation with the total negative charge of the anion, and expressing the formula as the simplest whole number ratio.
- ❖ The Group 7 halide ion, X^- , can be fluoride F^- , chloride Cl^- , bromide Br^- and iodide I^- .
- ❖ The ethanoate ion is included as an illustration of carboxylic acid salts ($RCOOH$ acid $\Rightarrow RCOO^-$ in salt).

The oxides, hydroxides and carbonates and hydrogencarbonates are usually white ionic solids and the Grp1 salts listed in the 2nd table are usually white/colourless crystalline ionic solids.

s-block cation \ anion	oxide	hydroxide	carbonate	hydrogencarbonate
	O^{2-}	OH^{-}	CO_3^{2-}	HCO_3^{-}
formula derived from Group1 cation M^{+}	M_2O	MOH	M_2CO_3	$MHCO_3$
	$(M^{+})_2O^{2-}$	$M^{+}OH^{-}$	$(M^{+})_2CO_3^{2-}$	$M^{+}HCO_3^{-}$

❖ There are also Group 1 hydrogen sulphates (hydrogensulfates/hydrogensulphates) of formula $MHSO_4$, i.e. half neutralised sulphuric acid which are rarely encountered but can be crystallised.

The oxidation numbers–states in the compounds listed in the two tables above and below:

- ❖ +1 for metal cation of group 1
- ❖ oxygen -2 , hydrogen $+1$, carbon $+4$ in table above and below
- ❖ halogens e.g. Cl -1 , nitrogen $+5$, sulphur $+6$
- ❖ you need to be able to analyse an anion to understand the relationship between the constituent oxidation states and the charge on the anion, **sum of oxidation states = overall charge on ion** e.g.
- ❖ carbonate, CO_3^{2-} , C is $+4$, 3 O's at -2 , sum of ox. states = $+4$ and $-6 = -2 =$ charge on anion
- ❖ hydrogencarbonate, HCO_3^- , H is $+1$, C is $+4$, 3 O's at -2 , sum of ox. states = $+1$ and $+4$ and $-6 = -1 =$ charge on anion
- ❖ nitrate(V), NO_3^- , N is $+5$, 3 O's at -2 , sum of ox. states = $+5$ and $-6 = -1 =$ charge on anion
- ❖ sulphate(VI), SO_4^{2-} , S is $+6$, 4 O's at -2 , sum of ox. states = $+6$ and $-8 = -2 =$ charge on anion

cation \ anion	halide	nitrate(V)	sulphate(VI)	ethanoate
	X^-	NO_3^-	SO_4^{2-}	CH_3COO^-
formula derived from Group 1 cation M^+	MX	MNO_3	$M_2SO_4^{2-}$	CH_3COOM
	M^+X^-	$M^+NO_3^-$	$(M^+)_2SO_4^{2-}$	$CH_3COO^-M^+$

- The three strong acids mentioned in reactions
- ❖ hydrochloric acid, $HCl \implies$ chloride salts
 - ❖ nitric acid, $HNO_3 \implies$ nitrate salts
 - ❖ sulphuric (or sulfuric) acid \implies sulphate salts (or sulfates)
 - ❖ and the 4th acid is the weak organic carboxylic acid **ethanoic acid***, $CH_3COOH \implies$ ethanoates
 - ❖ *old name 'acetic acid', and the salts were called 'acetates'