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LECTURE- PERIODIC PROPERTIES OF ELEMENTS  
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# Periodic Table of the Elements

Periodic Table of the Elements																		18
1 <b>H</b> Hydrogen 1.01																	2 <b>He</b> Helium 4.00	
3 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.01											5 <b>B</b> Boron 10.81	6 <b>C</b> Carbon 12.01	7 <b>N</b> Nitrogen 14.01	8 <b>O</b> Oxygen 16.00	9 <b>F</b> Fluorine 19.00	10 <b>Ne</b> Neon 20.18	
11 <b>Na</b> Sodium 22.99	12 <b>Mg</b> Magnesium 24.31											13 <b>Al</b> Aluminum 26.98	14 <b>Si</b> Silicon 28.09	15 <b>P</b> Phosphorus 30.97	16 <b>S</b> Sulfur 32.06	17 <b>Cl</b> Chlorine 35.45	18 <b>Ar</b> Argon 39.95	
19 <b>K</b> Potassium 39.10	20 <b>Ca</b> Calcium 40.08	21 <b>Sc</b> Scandium 44.96	22 <b>Ti</b> Titanium 47.88	23 <b>V</b> Vanadium 50.94	24 <b>Cr</b> Chromium 51.99	25 <b>Mn</b> Manganese 54.94	26 <b>Fe</b> Iron 55.85	27 <b>Co</b> Cobalt 58.93	28 <b>Ni</b> Nickel 58.69	29 <b>Cu</b> Copper 63.55	30 <b>Zn</b> Zinc 65.38	31 <b>Ga</b> Gallium 69.72	32 <b>Ge</b> Germanium 72.63	33 <b>As</b> Arsenic 74.92	34 <b>Se</b> Selenium 78.97	35 <b>Br</b> Bromine 79.90	36 <b>Kr</b> Krypton 84.80	
37 <b>Rb</b> Rubidium 85.47	38 <b>Sr</b> Strontium 87.62	39 <b>Y</b> Yttrium 88.91	40 <b>Zr</b> Zirconium 91.22	41 <b>Nb</b> Niobium 92.91	42 <b>Mo</b> Molybdenum 95.95	43 <b>Tc</b> Technetium 98.91	44 <b>Ru</b> Ruthenium 101.07	45 <b>Rh</b> Rhodium 102.91	46 <b>Pd</b> Palladium 106.42	47 <b>Ag</b> Silver 107.87	48 <b>Cd</b> Cadmium 112.41	49 <b>In</b> Indium 114.82	50 <b>Sn</b> Tin 118.71	51 <b>Sb</b> Antimony 121.76	52 <b>Te</b> Tellurium 127.6	53 <b>I</b> Iodine 126.90	54 <b>Xe</b> Xenon 131.29	
55 <b>Cs</b> Cesium 132.91	56 <b>Ba</b> Barium 137.33	57-71 Lanthanides	72 <b>Hf</b> Hafnium 178.49	73 <b>Ta</b> Tantalum 180.95	74 <b>W</b> Tungsten 183.85	75 <b>Re</b> Rhenium 186.21	76 <b>Os</b> Osmium 190.23	77 <b>Ir</b> Iridium 192.22	78 <b>Pt</b> Platinum 195.08	79 <b>Au</b> Gold 196.97	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.38	82 <b>Pb</b> Lead 207.20	83 <b>Bi</b> Bismuth 208.98	84 <b>Po</b> Polonium [208.98]	85 <b>At</b> Astatine 209.98	86 <b>Rn</b> Radon 222.02	
87 <b>Fr</b> Francium 223.02	88 <b>Ra</b> Radium 226.03	89-103 Actinides	104 <b>Rf</b> Rutherfordium [261]	105 <b>Db</b> Dubnium [262]	106 <b>Sg</b> Seaborgium [266]	107 <b>Bh</b> Bohrium [264]	108 <b>Hs</b> Hassium [269]	109 <b>Mt</b> Meitnerium [278]	110 <b>Ds</b> Darmstadtium [281]	111 <b>Rg</b> Roentgenium [280]	112 <b>Cn</b> Copernicium [285]	113 <b>Nh</b> Nihonium [286]	114 <b>Fl</b> Flerovium [289]	115 <b>Mc</b> Moscovium [289]	116 <b>Lv</b> Livermorium [293]	117 <b>Ts</b> Tennessine [294]	118 <b>Og</b> Oganesson [294]	
57 <b>La</b> Lanthanum 138.91	58 <b>Ce</b> Cerium 140.12	59 <b>Pr</b> Praseodymium 140.91	60 <b>Nd</b> Neodymium 144.24	61 <b>Pm</b> Promethium 144.91	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.96	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.93	66 <b>Dy</b> Dysprosium 162.50	67 <b>Ho</b> Holmium 164.93	68 <b>Er</b> Erbium 167.26	69 <b>Tm</b> Thulium 168.93	70 <b>Yb</b> Ytterbium 173.06	71 <b>Lu</b> Lutetium 174.97				
89 <b>Ac</b> Actinium 227.03	90 <b>Th</b> Thorium 232.04	91 <b>Pa</b> Protactinium 231.04	92 <b>U</b> Uranium 238.03	93 <b>Np</b> Neptunium 237.05	94 <b>Pu</b> Plutonium 244.06	95 <b>Am</b> Americium 243.06	96 <b>Cm</b> Curium 247.07	97 <b>Bk</b> Berkelium 247.07	98 <b>Cf</b> Californium 251.08	99 <b>Es</b> Einsteinium [254]	100 <b>Fm</b> Fermium 257.10	101 <b>Md</b> Mendelevium 258.10	102 <b>No</b> Nobelium 259.10	103 <b>Lr</b> Lawrencium [262]				

Alkali Metal

Alkaline Earth

Transition Metal

Basic Metal

Metalloid

Nonmetal

Halogen

Noble Gas

Lanthanide

Actinide

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## Periodic properties of the elements

Almost all trends in the properties of the elements can be traced to the electronic configuration of the atoms and atomic radii, and their variation with atomic number.

### Valence electron configurations

The valence electron configuration of the ground state of an atom of an element can be inferred from its group number. For example, in Group 1 all the elements have an  $ns^1$  valence configuration, where  $n$  is the period number. The valence electron configurations vary with group number as follows:

1	2	13	14	15	16	17	18
$ns^1$	$ns^2$	$ns^2np^1$	$ns^2np^2$	$ns^2np^3$	$ns^2np^4$	$ns^2np^5$	$ns^2np^6$

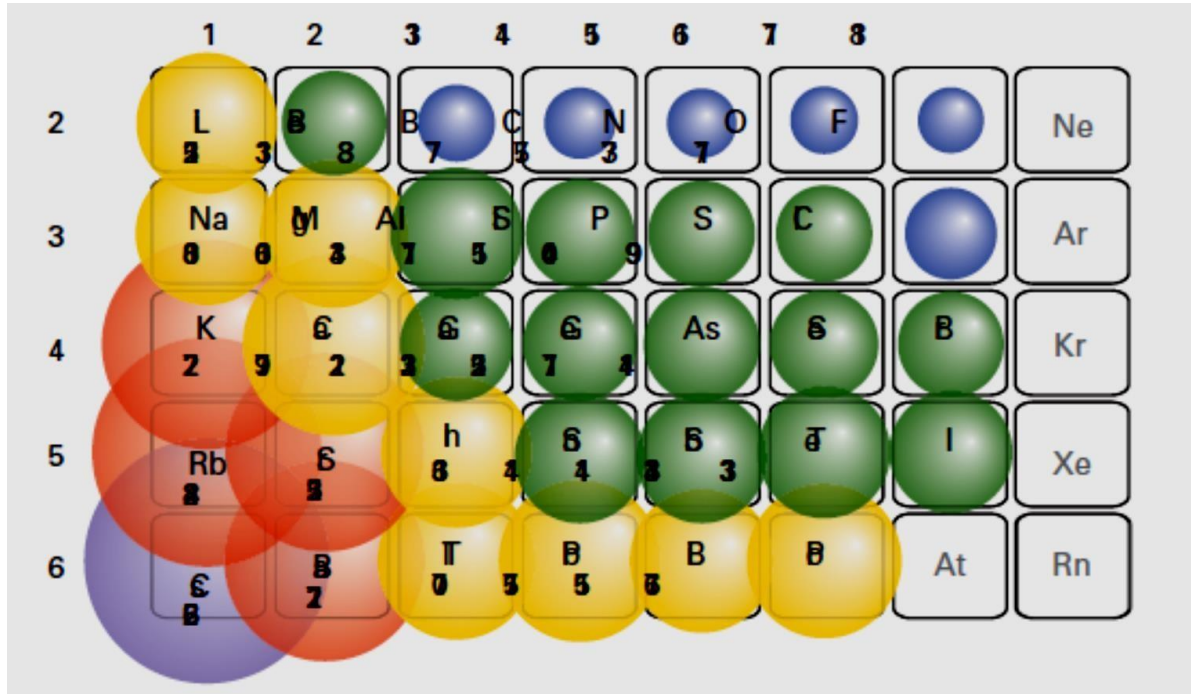
Electron configurations in the d block involve the filling of the  $(n - 1)d$  orbitals. In Period 4 they are as follows:

3	4	5	6	7	8	9	10	11	12
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$

Electron configurations with half-filled and full d subshells are favoured.

## Atomic parameters

Atomic radii increase down a group and, within the s and p blocks, decrease from left to right across a period.



The variation of atomic radii (in picometres) through the main groups of the periodic table.

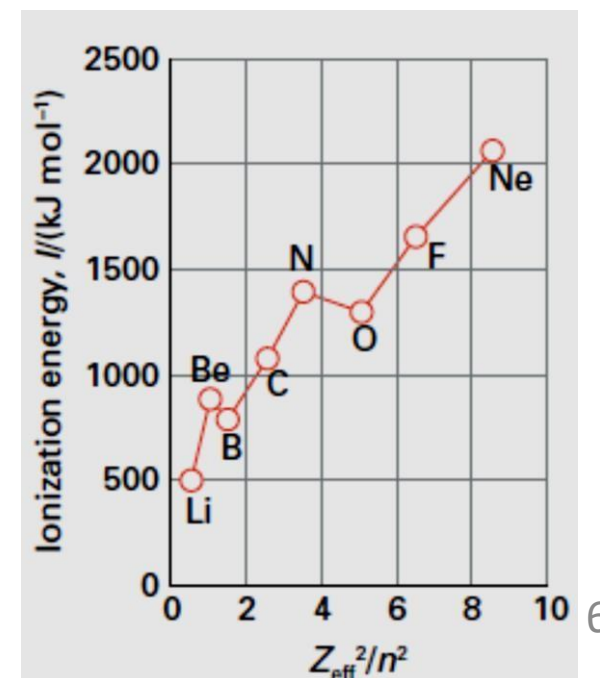
- **Atomic radii increase down a group and decrease from left to right across a period.** Across a period, as a result of the joint effects of penetration and shielding, there is an increase in effective nuclear charge. This increase draws in the electrons and results in a smaller atom.
- On descending a group, electrons occupy successive shells outside a completed core and the radii increase.
- **Atomic radii in the 5d series of the d block are very similar to their congeners in the 4d series even though the atoms have a greater number of electrons.** For example, the radii of Mo and W in Group 6 are 140 and 141 pm, respectively. This reduction of radius below that expected, the *lanthanide contraction*, is due to the presence of 4f electrons in the intervening lanthanoids: the poor shielding properties of f electrons results in a higher effective nuclear charge

#### **(b) Ionization energies and electron affinities**

- Ionization energy increases across a period and decreases down a group.
- Electron affinities are highest for elements near fluorine, particularly the halogens.

## Ionization energies

- The ionization energy of an element is the energy required to remove an electron from a gas-phase atom. Ionization energies correlate strongly with atomic radii, and elements that have small atomic radii generally have high ionization energies.
- Therefore, as the atomic radius increases down a group, the ionization energy decreases. Likewise, the decrease in radius across a period is accompanied by an increase in ionization energy
- The energies of electrons in hydrogenic atoms are proportional to  $Z_{\text{eff}}^2/n^2$ , where  $Z_{\text{eff}}$  is the effective nuclear charge.
- Plots of first ionization energies against  $Z_{\text{eff}}^2/n^2$  for the outermost electrons for the elements Li to Ne ( $n = 2$ ) is shown here.



## Electron Affinities

Electron affinity of an element is defined as the amount of energy released in adding an extra electron from outside to an isolated neutral gaseous atom in its lowest energy state ( i.e. ground state) to convert it into a gaseous anion.



If the additional electron can enter a shell where it experiences a strong effective nuclear charge, an element has a high electron affinity. Therefore, elements close to F (other than the noble gases) have the highest electron affinities as  $Z_{\text{eff}}$  is then large.

The addition of an electron to a singly charged ion (as in the formation of  $\text{O}^{2-}$  from  $\text{O}^-$ ) is endothermic as it takes energy to push an electron on to a negatively charged species.

**Electron affinities are highest for elements near fluorine, particularly the halogens.**

## Electronegativity

- The electronegativity, is the power of an atom of the element to attract electrons to itself when it is part of a compound.
- The Mulliken definition of electronegativity is the mean of the ionization energy and electron affinity of an element.
- If an atom has a high ionization energy (so it is unlikely to give up electrons) and a high electron affinity (so there are energetic advantages in its gaining electrons), then it is more likely to attract an electron to itself.
- Consequently, **the electronegativities of the elements increase left to right across a period and decrease down a group**

There are some exceptions to this general trend as can be seen from the following electronegativities:

<b>Al</b>	<b>Si</b>
1.61	1.90
<b>Ga</b>	<b>Ge</b>
1.81	2.01
<b>In</b>	<b>Sn</b>
1.78	1.96

This departure from a smooth decrease down the group is called the **alternation effect** and is due to the intervention of the 3d subshell earlier in Period 4.

The term ‘electropositive’, which describes an element’s ability to lose electrons.



## Diagonal relationships

- The element at the head of each group possesses a diagonal relationship with the element to its lower right. Diagonal relationships arise because the atomic radii, charge densities, electronegativities, and hence many of the chemical properties, of the two elements are similar.
- The most striking diagonal relationships are those between Li and Mg. For example, whereas the Group 1 elements form compounds that are essentially ionic in nature, Li and Mg salts have some degree of covalent character in their bonding.
- There is a strong diagonal relationship between Be and Al: both elements form covalent hydrides, halides, and oxides.
- The diagonal relationship between B and Si is illustrated by the fact that both elements form flammable, gaseous hydrides whereas aluminium hydride is a solid.

The atomic radius, and hence some chemical properties, of some Period 2 elements is similar to that of the element to their lower right in the periodic table.

	1	2	13	14
2	Li 157	Be 112	B 88	C
3	Na	Mg 160	Al 143	Si 118

(a)

	1	2	13	14
2	Li 0.98	Be 1.57	B 2.04	C
3	Na	Mg 1.31	Al 1.61	Si 1.90

Fig 1: The diagonal relationship between (a) atomic radii (in picometres) and (b) Pauling electronegativity in Periods 2 and 3.

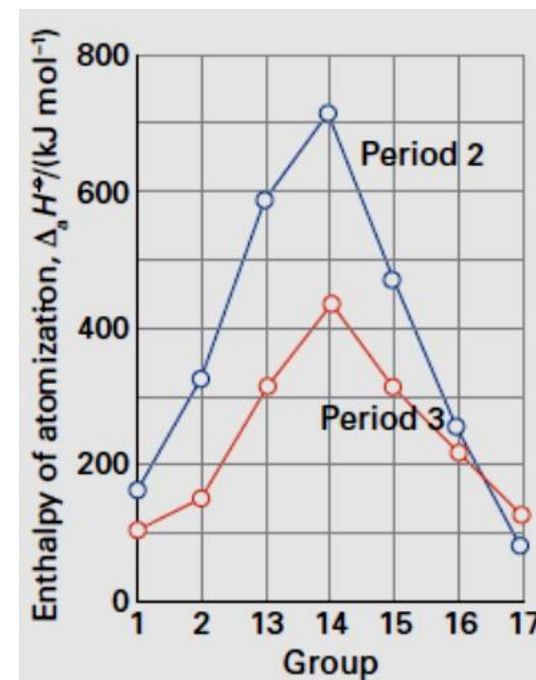


Fig 2: Variation of the enthalpy of atomization in the s- and p-block elements.

## Enthalpies of atomization

- The enthalpy of atomization of an element,  $\Delta_a H^\circ$ , is a measure of the energy required to form gaseous atoms. For solids, the enthalpy of atomization is the enthalpy change associated with the atomization of the solid; for molecular species, it is the enthalpy of dissociation of the molecules.
- The enthalpies of atomization first increase and then decrease across Periods 2 and 3, reaching a maximum at C in Period 2 and Si in Period 3.

- The enthalpies of atomization of the d-block elements are higher than those of the s- and p-block elements, in line with their greater number of valence electrons and consequently stronger bonding.
- The values reach a maximum at Groups 5 and 6 (Fig. 3), where there is a maximum number of unpaired electrons available to form bonds.
- The middle of each row shows an irregularity due to spin correlation, which favours a half filled d shell for the free atom. This effect is particularly evident for the 3d series, in which Cr ( $3d^5 4s^1$ ) and Mn ( $3d^5 4s^2$ ).
- The enthalpy of atomization decreases down a group in the s and p blocks but increases down a group in the d block.
- Thus s and p orbitals become less effective at forming bonds as the period number increases, whereas d orbitals become more effective. These trends are attributed to the expansion of p orbitals on descending a group from optimal for overlap to too diffuse for extensive overlap and, in contrast, d orbitals expanding in size from too contracted to optimal for overlap.
- The same trends can be seen in the melting points of the elements, where a greater number of valence electrons leads to greater binding energy and a higher melting temperature.

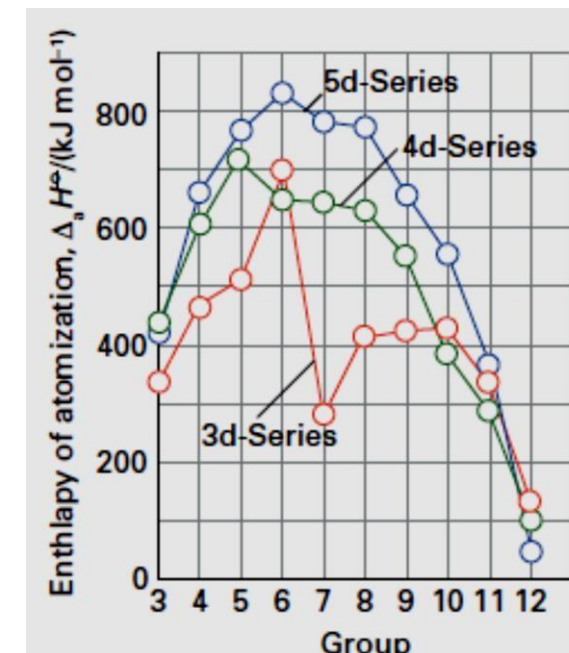


Fig 3: Variation of enthalpy of atomization in the d-block elements

## Hard and soft acids and bases

According to **HSAB** principle, the Lewis acids and bases can be further divided into hard or soft or borderline types.

**Hard Lewis acids** are characterized by small ionic radii, high positive charge, strongly solvated.

**Soft Lewis acids** are characterized by large ionic radii, low positive charge.

**Hard Lewis bases** are characterized by small ionic radii, strongly solvated, highly electronegative, weakly polarizable.

**Soft Lewis bases** are characterized by large ionic radii, intermediate electronegativity, highly polarizable.

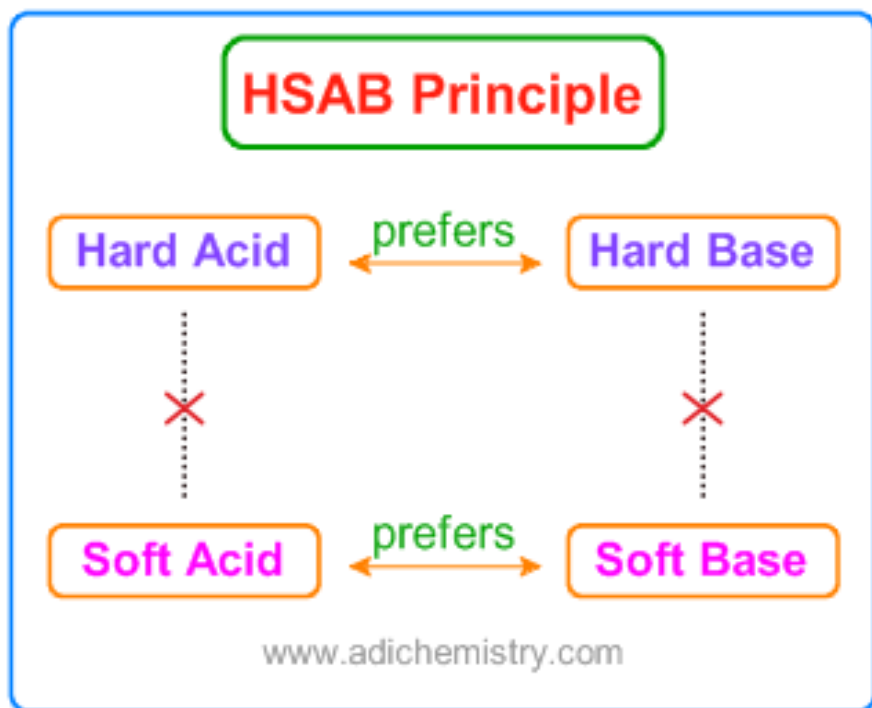
The **Borderline** Lewis acids and bases have intermediate properties.

*In short, Hard acids and bases are small and non-polarizable, whereas Soft acids and bases are larger and more polarizable.*

**HSAB Principle:** Hard acids tend to bind to hard bases and soft acids tend to bind to soft bases.

Hard acids bond in the order:  $I^- < Br^- < Cl^- < F^-$ .

Soft acids bond in the order:  $F^- < Cl^- < Br^- < I^-$ .



Hard	Borderline	Soft
<i>Acids</i>		
$H^+, Li^+, Na^+, K^+$	$Fe^{2+}, Co^{2+}, Ni^{2+}$	$Cu^+, Au^+, Ag^+, Tl^+, Hg_2^{2+}$
$Be^{2+}, Mg^{2+}, Ca^{2+}$	$Cu^{2+}, Zn^{2+}, Pb^{2+}$	$Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}$
$Cr^{2+}, Cr^{3+}, Al^{3+}$	$SO_2, BBr_3$	$BH_3$
$SO_3, BF_3$		
<i>Bases</i>		
$F^-, OH^-, H_2O, NH_3$	$NO_2^-, \underline{SO_3}^{2-}, Br^-$	$H^-, R^-, \underline{CN}^-, CO, I^-$
$\underline{CO_3}^{2-}, NO_3^-, O^{2-}$	$\underline{N_3}^-, N_2$	$\underline{SCN}^-, R_3P, C_6H_5$
$\underline{SO_4}^{2-}, \underline{PO_4}^{3-}, ClO_4^-$	$C_6H_5N, \underline{SCN}^-$	$R_2S$
* The underlined element is the site of attachment to which the classification refers.		

## Occurrence

- Soft acids tend to bond to soft bases and hard acids tend to bond to hard bases.
- Hard hard and soft soft interactions help to systematize the terrestrial distribution of the elements.
- These tendencies explain certain aspects of the **Goldschmidt classification** of the elements into four types :

**Lithophiles** are found primarily in the Earth's crust (the lithosphere) in silicate minerals, and include Li, Mg, Ti, Al, and Cr (as their cations). These cations are hard, and are found in association with the hard base  $O^{2-}$ .

**Chalcophiles** are often found in combination with sulfide (and selenide and telluride) minerals, and include Cd, Pb, Sb, and Bi. These elements (as their cations) are soft, and are found in association with the soft base  $S^{2-}$  (or  $Se^{2-}$  and  $Te^{2-}$ ). Zinc cations are borderline hard, but softer than  $Al^{3+}$  and  $Cr^{3+}$ , and Zn is also often found as its sulfide.

**Siderophiles** are intermediate in terms of hardness and softness and show an affinity for both oxygen and sulfur. They occur mainly in their elemental state and include Pt, Pd, Ru, Rh, and Os.

**Atmophiles** are gases such as H, N, and Group 18 elements (the noble gases).

## **Metallic character**

- The chemical properties of the metallic elements can be considered as arising from the ability of the elements to lose electrons to form the electron sea that binds together the cations and accounts for metallic bonding.
- Elements with low ionization energies are likely to be metals and those with high ionization energies are likely to be nonmetals. Thus, as ionization energies decrease down a group the elements become more metallic, and as the ionization energies increase across a row the elements become less metallic.
- These trends can also be directly related to the trends in atomic radii as large atoms typically have low ionization energies and are more metallic in character.
- In Group 15: N and P are nonmetals, As exists as nonmetal, metalloid, and metallic allotropes, and Sb and Bi are metals.

**The metallic character of the elements decreases across a period and increases down a group. Many elements in the p block exist as allotropes.**

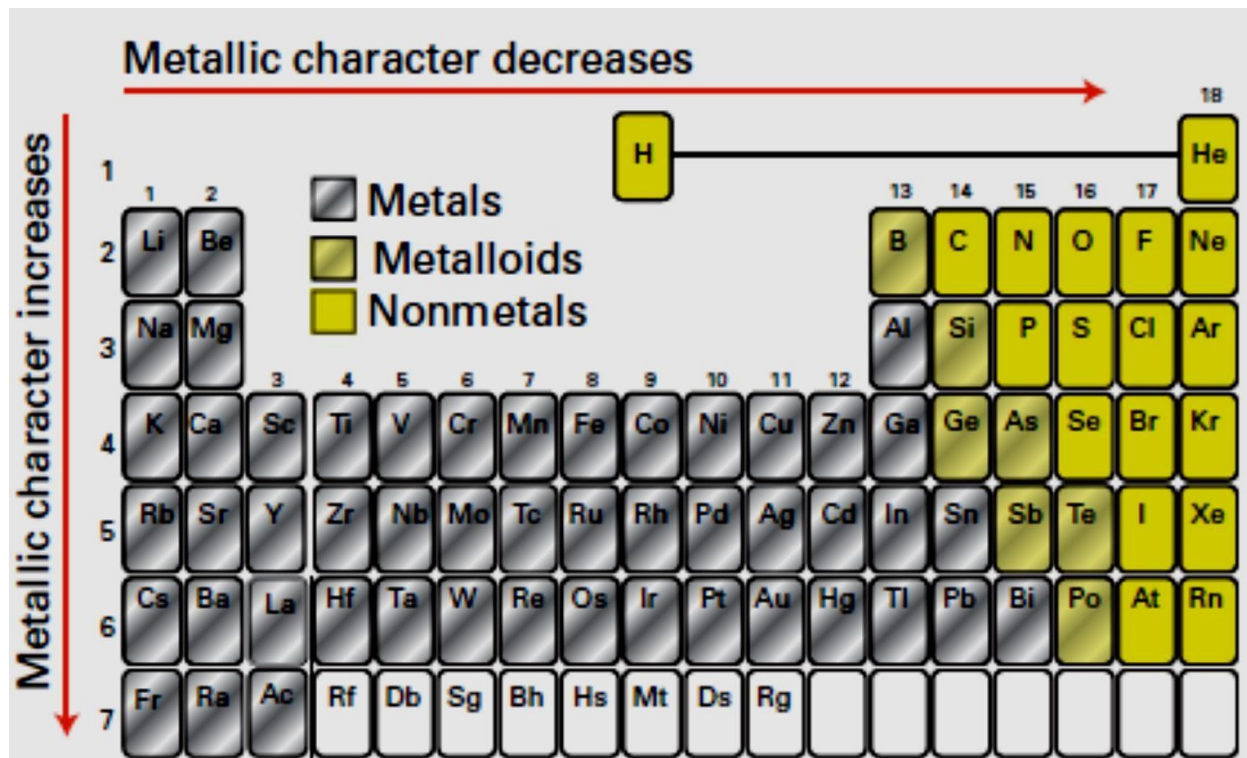


Fig 4: The variation of metallic character through the periodic table.



## Oxidation states

- A complete or half-full valence shell imparts greater stability than a partially filled shell. Therefore, there is a tendency for atoms to gain or lose electrons until they acquire that configuration.
- In Groups 1, 2, and 13, the oxidation numbers are +1, +2, and +3, respectively.
- From Group 14 to Group 17 it becomes increasingly energetically favourable—for the atoms to accept electrons in order to complete the valence shell. Consequently, the group oxidation numbers are -4, -3, -2, -1 with more electronegative elements.
- Group 18 elements already have a complete octet of electrons and are neither readily oxidized nor reduced.
- The relative stability of an oxidation state in which the oxidation number is 2 less than the group oxidation number is an example of the *inert pair effect*. The heavier elements of the p block also form compounds with the element with an oxidation number 2 less than the group oxidation number.
- For example, in Group 13 whereas the group oxidation number is +3, the +1 oxidation state increases in stability down the group. In fact, the most common oxidation state of thallium is Tl(I).
- This effect is often ascribed to the large energy that is needed to remove the  $ns^2$  electrons after the  $np^1$  electron has been removed. Another contribution to the effect may be the low MX bond enthalpies for the heavier p-block elements and the decreasing lattice energy as the atomic radii increase down a group.

## Periodic characteristics of compounds

### Coordination numbers

**Low coordination numbers generally dominate for small atoms; high coordination numbers are possible as a group is descended.**

- In the p block, low coordination numbers are most common for the compounds of Period 2 elements but higher coordination numbers are observed as each group is descended and the radius of the central atom increases.
- For example, in Group 15 N forms three-coordinate molecules such as  $\text{NCl}_3$  and four-coordinate ions such as  $\text{NH}_4^+$ , whereas its congener P forms molecules with coordination numbers of 3 and 5, as in  $\text{PCl}_3$  and  $\text{PCl}_5$ , and six-coordinate ionic species such as  $\text{PCl}_6^-$ . This higher coordination number in Period 3 elements is an example of hypervalence and is sometimes attributed to the participation of d orbitals in bonding.
- In the d block the 4d and 5d series of elements tend to exhibit higher coordination numbers than the 3d series elements due to their larger radii. For example, in Group 3 Sc forms the 6-coordinate  $\text{ScF}_6^{3-}$  ion whereas La forms the fluoride-bridged 9-coordinate  $\text{LaF}_9^{6-}$  ion. Very high coordination numbers have been observed for some large atoms, for example Th forms the 10-coordinate  $[\text{Th}(\text{C}_2\text{O}_4)_4(\text{OH}_2)_2]^{4-}$  ion.

## Bond enthalpy trends

The mean bond enthalpy is the average bond dissociation enthalpy taken over a series of compounds. In the p block, E-H bonds get weaker on descending a group whereas in the d block they get stronger. These trends are attributed to the same orbital contraction and expansion effects as affect atomization enthalpies.

Smaller atoms form stronger bonds because the shared electrons are closer to each of the atomic nuclei. The strength of the Si-Cl bond is attributed to the fact that the atomic orbitals of the two elements have similar energies and efficient overlap. High values are also sometimes attributed to a contribution from  $\pi$ -bonding involving d orbitals.

$B/(\text{kJ mol}^{-1})$		$B/(\text{kJ mol}^{-1})$	
C–C	348	C–Cl	338
Si–Si	226	Si–Cl	391
Ge–Ge	188	Ge–Cl	342

- Bond enthalpies E-H for p-block elements decrease down a group whereas in the d block they increase.
- For an atom E that has no lone pairs, the EX bond enthalpy decreases down the group;
- for an atom that has lone pairs, it typically increases between Periods 2 and 3, and then decreases down the group.

In the d block, bond enthalpies generally increase down a group, a trend that is the opposite of the general trend for the p block:

$B/(\text{kJ mol}^{-1})$		$B/(\text{kJ mol}^{-1})$	
Co-H	226	Fe-C	390
Rh-H	247	Ru-C	528
		Os-C	598

d orbitals appear to become more effective at forming bonds down a group as they expand in size from contracted to optimal for overlap, and unpaired electrons become much more common.

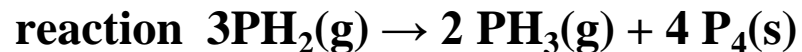
**Elemental sulfur forms rings or chains with S-S single bonds, whereas oxygen exists as diatomic molecules.**

We need to consider the relative magnitude of the bond enthalpies for the single and double bonds:

$B/(\text{kJ mol}^{-1})$	$B/(\text{kJ mol}^{-1})$
O-O 142	O=O 498
S-S 263	S=S 431

Because an O=O bond is more than three times as strong as an O-O bond, there is a much stronger tendency for oxygen to form O=O bonds than O-O bonds, as in dioxygen, O<sub>2</sub>. An S=S bond is less than twice as strong as an S-S bond, so the tendency to form S=S bonds is not as strong as in oxygen and the formation of S-S bonds is more likely.

**Another example is the disproportionation**



**The origin of the spontaneity of this reaction is the strength of the P-P bonds in molecular phosphorus,  $\text{P}_4$ .**

**There are the same number (six) of P-H bonds in the reactants as there are in the products, but the reactants have no P-P bonds.**

### **Anomalies**

The first member of each group within the p block shows differences from the rest of the group that are attributed to smaller atomic radii and a lack of low-lying d orbitals.

- For example, in Group 14 carbon forms a number of catenated hydrocarbons and also strong multiple bonds in the alkenes and alkynes. This tendency to catenation is much reduced for its congeners with longest silane formed contains just four Si atoms.
- Nitrogen shows distinct differences from phosphorus and the rest of Group 15. Thus, nitrogen commonly exhibits a coordination number of 3, as in  $\text{NF}_3$ , and a coordination number of 4 in species such as  $\text{NH}_4^+$  and  $\text{NF}_4^+$  whereas phosphorus can form 3- and 5-coordinate compounds, such as  $\text{PF}_3$  and  $\text{PF}_5$ , and 6-coordinate species such as  $\text{PF}_6^-$ .

- The extent of hydrogen bonding is much greater in the compounds of the first member of each group. For example, the boiling point of ammonia is  $-33^{\circ}\text{C}$ , which is higher than that of the other Group 15 hydrides.
- Likewise, water and hydrogen fluoride are liquids at room temperature whereas  $\text{H}_2\text{S}$  and  $\text{HCl}$  are gases.
- The 3d metals form compounds with lower coordination numbers and oxidation states than the 4d and 5d elements.
- For example, the most stable oxidation state of chromium is Cr(III) whereas it is M(VI) for Mo and W.
- The dihalides of the 3d-series elements are mostly ionic solids, as in  $\text{CrF}_2$ , whereas the 4d- and 5d-series elements form higher halides such as  $\text{MoF}_6$  and  $\text{WF}_6$ , which are liquids at room temperature.
- These differences are attributable to the smaller ionic radii of the 3d-series elements and the fact that the radii of the 4d- and 5d-series elements are quite similar (due to lanthanide contraction).

The oxidation state Ln(III) dominates in compounds of the lanthanoids, whereas the actinoids exhibit a variety of oxidation states.

The elements Ce to Lu are all highly electropositive. The elements favour the oxidation state Ln(III). For example, the radii of Ln<sup>3+</sup> ions contract steadily across the series. This decrease is attributed in part to the increase in  $Z_{\text{eff}}$  as electrons are added to the 4f subshell.

The elements from thorium (Th,  $Z = 90$ ) to lawrencium (Lr,  $Z = 103$ ) have ground-state electron configurations that involve the filling of the 5f subshell, and in this sense are analogues of the lanthanoids.

Like the lanthanoids, the actinoids have large atomic and ionic radii and as a result often have high coordination numbers. For example, U in solid  $\text{UCl}_4$  is 8-coordinate and in solid  $\text{UBr}_4$  it is 7-coordinate in a pentagonal-bipyramidal array.

# Hydrides of the elements

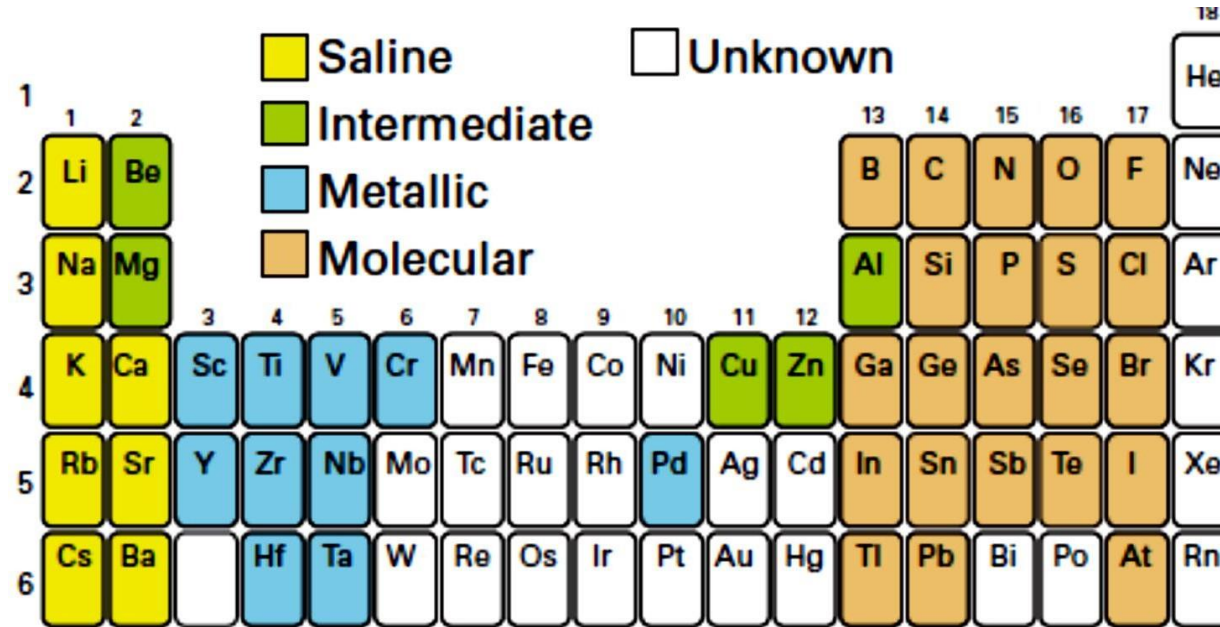


Fig 5: Classification of the binary hydrides of the s-, p-, and d-block elements.

- Molecular compounds of hydrogen are common for the nonmetallic, electronegative elements of Groups 13 to 17; some examples are  $\text{B}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$ . These covalent hydrides are gases, with the exception of water (due to extensive hydrogen bonding).
- The saline hydrides are formed by the electropositive elements of Group 1 and Group 2 (with the exception of Be). The saline hydrides are ionic solids with high melting points.
- Nonstoichiometric metallic hydrides are formed by all the d-block metals of Groups 3, 4, and 5, and by the f-block elements.



## Oxides of the elements

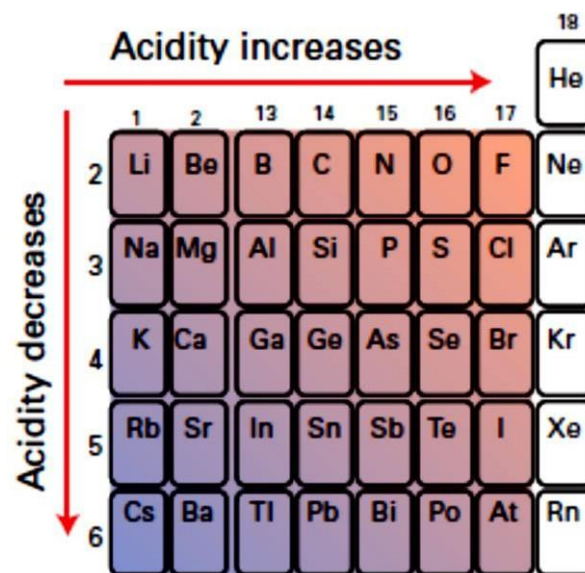
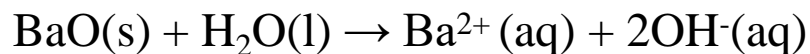
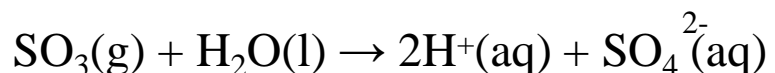


Fig 6: The general variation of acidic nature of the oxides of the elements through the periodic table.

**Metals typically form basic oxides.** The electropositive metal forms a cation readily and the oxide anion abstracts a proton from water. For example, OH ions are produced when barium oxide reacts with water:



**Nonmetals form acidic oxides.** The electronegative element pulls in electrons from coordinated H<sub>2</sub>O molecules, liberating H<sup>+</sup>. For example, sulfur trioxide reacts with water to produce hydronium ions :



- The acidic nature of the oxides increases across a row and decreases down a group for a given oxidation state (Fig. 6).
- In Group 13 the element at the head of the group, B, is a nonmetal and forms the acidic oxide  $B_2O_3$ . At the bottom of the group the metallic character has increased and the inert pair effect has reduced the stable oxidation state from 3 to 1 and the oxide of thallium is the basic  $Tl_2O$ .
- Metals form basic oxides and nonmetals form acidic oxides. The elements form normal oxides, peroxides, superoxides, suboxides, and nonstoichiometric oxides.

### **Halides of the elements**

- With the exception of Li and Be, the s-block halides are ionic and the p-block fluorides are predominantly covalent.
- The d-block elements form halides with a range of oxidation states. The higher oxidation state halides are formed with F and Cl. The lower oxidation state halides are ionic solids. The higher oxidation state chlorides formed predominantly by the 4d- and 5d-series elements are covalent and there is an increased tendency to form cluster compounds with metalmetal bonds.
- In the d block, low oxidation state halides tend to be ionic and high oxidation state halides tend to be covalent.

## Home Assignment

1. Arrange the following in increasing order of their ionisation energies and justify the answer.

Li, Be, B, C, N, O, F, Ne

2. Give the Mulliken's definition of electronegativity. Arrange the halogens in decreasing order of their electronegativity and electron affinity.

3. Why the common ores of Ni and Cu are sulfides but Al is obtained from the oxide and Ca from the carbonate?

Hint: HSAB Principle

4. Arrange the following in increasing order of metallic character.

B, Al, Mg, K

5. In the II period, the most acidic oxide is formed by which element

a. F b. N c. O d. Li

### References:

1. Peter Atkins, Tina Overton, Jonathan Rourke, Mark Weller, Fraser Armstrong, Mike Hagerman; Shriver & Atkins' Inorganic Chemistry, 5th Ed. 2012
2. J. E. Huheey, E. A. Keiter and R. L. Keiter, O. K. Medhi, Inorganic Chemistry: Principle of structure and reactivity, 4th Ed., Pearson Education, 2006.