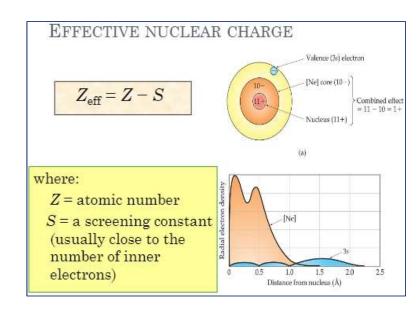


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# FROM MENDELEEV TO MOSELEY

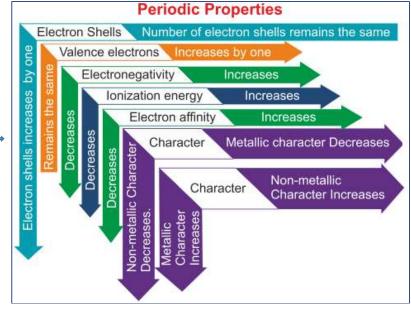
- 1869: Mendeleev
  - arranged elements by atomic mass
  - Noted similarities, forced to leave holes in PT
- o 1913: Moseley
  - Developed concept of atomic numbers
  - Bomabrded elements with high-energy electrons
     Unique frequency
  - Correctly identified atomic number as number of protons



Based on atomic number.

Position of elements are related to electronic configuration.

Periodic properties shows gradual variation at regular intervals.



#### Quantum numbers

the four are

- principle (energy) n = 1,2,3...
- azimuthal (shape) I = 0,1, 2... n-1
- magnetic (orientation) m<sub>i</sub> = -1,...0,...+1
  - spin (differentiates two electrons in same orbital) (±1/2)

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Course Instructor: **Dr Bhar Saha** Dept. of Science & Maths IIITG, Guwahati The physical and chemical properties of the elements vary with atomic number with regularity. All trends in the properties of the elements are related to the electronic configuration of the atoms and atomic radii, and their variation with atomic number. These periodic properties of the elements are:

- Valence electron configurations
- Atomic parameters
- Occurrence
- Metallic character
- Oxidation states

Periodic characteristics of compounds are

- Coordination numbers
- Bond enthalpy trends
- Anomalies
- Binary compounds
- Wider aspects of periodicity

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# 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 ns1 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

ns1 ns2 ns2np1 ns2np2 ns2np3 ns2np4 ns2np5 ns2np6

Electron configurations in the d block are slightly less systematic, but 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

3d1 4s2 3d2 4s2 3d3 4s2 3d5 4s1 3d5 4s2 3d6 4s2 3d7 4s2 3d8 4s2 3d10 4s1 3d10 4s2

Half-filled and full d subshells are favoured.

Isoelectronic species have the same electronic configuration. (Na+, Ne, F-)

Therefore, they must be **distinguished by** the number of **protons** present.

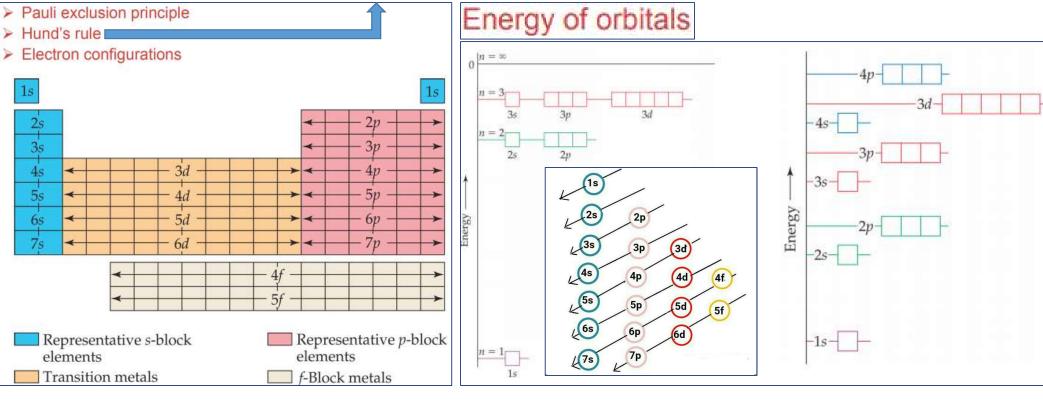
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Element	Element Configuration		C	Noble gas			
Li	1s <sup>2</sup> 2s <sup>1</sup>	†↓	1	[He]2s <sup>1</sup>			
		1s	2s		2p		
Be	1s <sup>2</sup> 2s <sup>2</sup>	<b>†</b> ‡	11				[He]2s <sup>2</sup>
		1s	2s		2p		
В	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>1</sup>	<b>†</b> ‡	11	<b>†</b>			[He]2s <sup>2</sup> 2p <sup>1</sup>
		1s	2s		2p		
C	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	ţţ	11	1	†		[He]2s <sup>2</sup> 2p <sup>2</sup>
		1s	2s		2p	100	
N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	11	11	1	†	1	[He]2s <sup>2</sup> 2p <sup>3</sup>
		1s	2s		2p		
0	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>4</sup>	11	11	11	1	1	[He]2s <sup>2</sup> 2p <sup>4</sup>
		1s	2s		2p		
F	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	<b>†</b> ‡	11	<b>†</b> ‡	†‡	1	[He]2s <sup>2</sup> 2p <sup>5</sup>
		1s	2s		2p		
Ne	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup>	†↓	†↓	ţţ	ţţ	11	[Ne]
		4-	0-		0-		

## Pauli exclusion principle: no 2 e⁻ can have same 4 #'s (must have opp. spin, ↑↓)

"For degenerate orbitals, the **lowest** energy is attained when the number of electrons with the same spin is maximized."



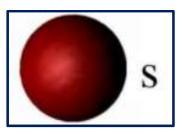
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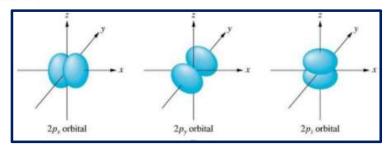
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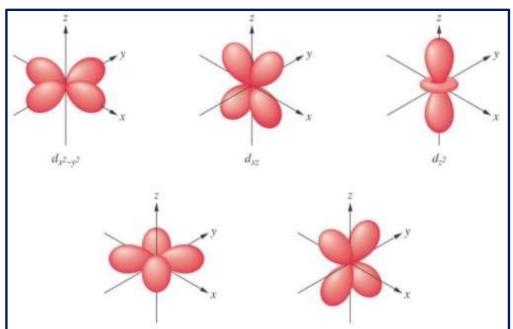
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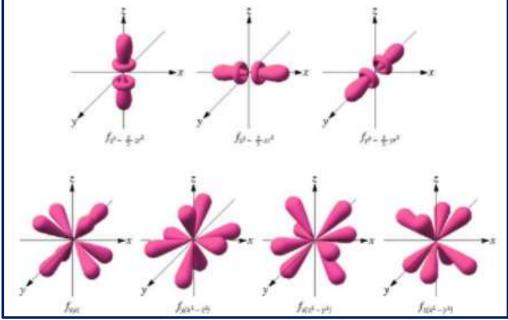
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# **Atomic Orbitals**









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

The radii of atoms and ions, and the energy changes associated with the formation of ions—vary periodically. 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. 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 than expected on the basis of a simple extrapolation from other atoms.

A similar contraction is found in the elements that follow the d block. For example, although there is a substantial increase in atomic radius between C and Si (77 and 118 pm, respectively), the atomic radius of Ge (122 pm) is only slightly greater than that of Si.

### 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.

We need to be aware of the energies needed to form cations and anions of the elements.

Ionization energies are relevant to the formation of cations; electron affinities are relevant to the formation of anions.

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. As discussed there are variations in this trend: in particular, high ionization energies occur when electrons are removed from half-filled or full shells or subshells.

Thus the first ionization energy of nitrogen ([He]2s2 2p3) is 1402 kJ mol<sup>-1</sup>, which is higher than the value for oxygen ([He]2s2 2p4, 1314 kJ mol<sup>-1</sup>). Similarly, the ionization energy of phosphorus (1011 kJ mol<sup>-1</sup>) is higher than that of sulfur (1000 kJ mol<sup>-1</sup>).

Element	$I_1$	$I_2$	$I_3$	$I_4$	$I_5$	$I_6$	$I_7$
Na	495	4562			(inner-sh	nell electrons)	
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

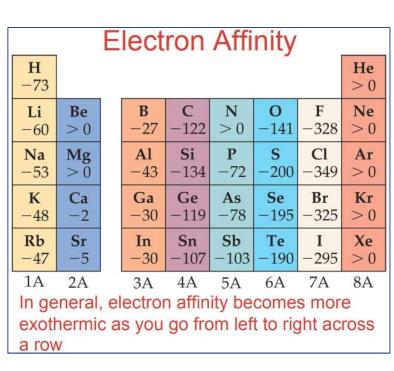
The energies of electrons in hydrogenic atoms are proportional to  $\mathbb{Z}^2/n^2$ .

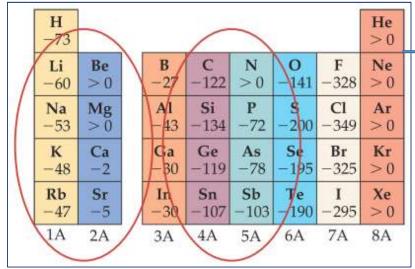
An element has a high electron affinity if the additional electron can enter a shell where it experiences a strong effective nuclear charge. Therefore, elements close to F (other than the noble gases) have the highest electron affinities as  $Z_{eff}$  is then large. The addition of an electron to a singly charged ion (as in the formation of  $O_2$  from O) is invariably negative (that is, the process is endothermic) because it takes energy to push an electron on to a negatively charged species.

➤ For atoms in the same group, Z<sub>eff</sub> is essentially the same, but the valence electrons are farther from the nucleus.

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There are two discontinuities in this trend

The first occurs between Groups IA and IIA

- ➤ Added electron must go in *p*-orbital, not *s*-orbital.
- Electron is farther from nucleus and feels repulsion from s-electrons.

The second occurs between Groups IVA and VA.

- Group VA has no empty orbitals.
- Extra electron must go into occupied orbital, creating repulsion.

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# **Electronegativity**

Electronegativity increases across a period and decreases down a group. Electronegativity is the power of an atom of the element to attract electrons to itself when it is part of a compound. Trends in electronegativity can be correlated with trends in atomic radii. This correlation is most readily understood in terms of the Mulliken definition of electronegativity as 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 electronegativity of the elements, tracking the trends in ionization energies and electron affinities, which in turn track atomic radii, typically increase left to right across a period

and decrease down a group. However, the Pauling values of electronegativity are commonly used.

Some exceptions to this general trend as can be seen from the following electronegativities:

Al	Si
1.61	1.90
Ga	Ge
1.81	2.01
In	Sn
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 alternation effect also appears in a more chemically direct manner, where it summarizes the nonexistence of various compounds in Groups 13 to 15, where unknown compounds like  $AsCl_5$  are unstable above -50°C.

Although electronic factors such as electronegativity no doubt play a role in these examples, steric effects are important too, especially for N.

The term 'electropositive', which describes an element's ability to lose electrons, needs to be used with caution. In some applications it means that the element has a low electronegativity;

in others it means that the redox couple  $M^{n+}/M$  has a strongly negative standard potential (so that M is a reducing metal).

# Diagonal relationships

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. Most of the trends in the chemical properties of the elements within the periodic table are best discussed in terms of vertical trends within groups or horizontal trends across periods.

The element at the head of each group also commonly possesses a diagonal relationship with the element to its lower right. Diagonal relationships arise because the atomic radii, charge densities, electronegativity, 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 analogous compounds of Group 2 are predominantly

ionic. 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.

# **Enthalpies of atomization**

The enthalpy of atomization increases with increasing number of <u>valence</u> electrons. The enthalpy of atomization of an element,  $\Delta_a H^O$ , 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. 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 values decrease between C and N, and Si and P: even though N and P each have five valence electrons, two of these electrons form a lone pair and only three are involved in bonding. A similar effect is seen between N and O, where O has six valence electrons of which four form lone pairs and only two are involved in bonding.

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, 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  $Cr(3d^54s^1)$  and  $Mn(3d^54s^2)$  have significantly lower atomization energies than expected from a simple consideration of their number of valence electrons.

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.

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#### Occurrence

Hard-hard and soft-soft interactions help to systematize the terrestrial distribution of the elements.

Some elements occur in their elemental state in nature, for example the gases nitrogen and oxygen, the nonmetal sulfur, and the metals silver and gold. Most elements however, occur naturally in ores as compounds with other elements.

The concept of hardness and softness helps to rationalize a great deal of

inorganic chemistry, including the type of compound that the element forms in Nature.

Thus, soft acids tend to bond to soft bases and hard acids tend to bond to hard bases.

These tendencies explain certain aspects of the **Goldschmidt classification** of the elements into four types, a scheme widely used in geochemistry:

**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  $O_2$ .

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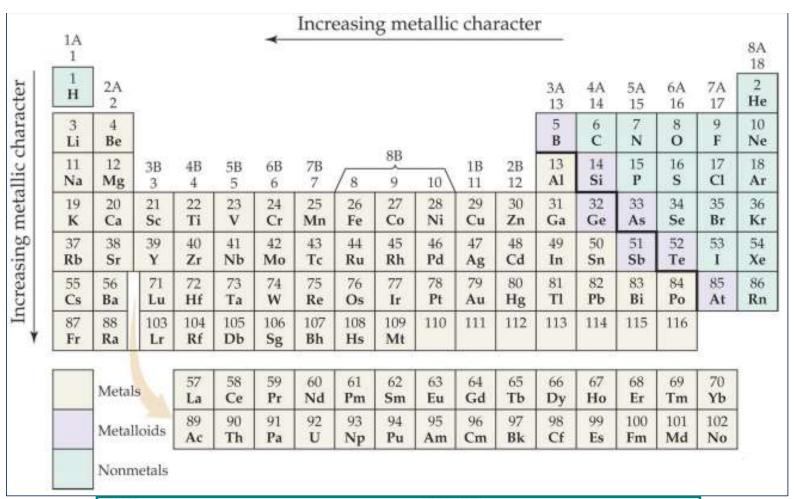
Course Instructor: **Dr Bhar Saha** Dept. of Science & Maths IIITG, Guwahati Chalcophiles are often found in combination with sulfide (and selenide and telluride) minerals, and include Cd, Pb, Sb, and Bi. These elements (as their cations) are soft, and are found in association with the soft base  $S_2$  (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

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

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. Consequently, 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. This trend is most noticeable within Groups 13 to 16, where the elements at the head of the group are nonmetals and those at the foot of the group are metals. Within this general trend there are allotropic variations in the sense that some elements exist as both metals and nonmetals. An example is Group 15: N and P are nonmetals, As exists as nonmetal, metalloid, and metallic allotropes, and Sb and Bi are metals. Elements in the p block typically form several allotropes



Metals	Nonmetals
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

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#### Oxidation states

The group oxidation number can be predicted from the electron configuration of an element.

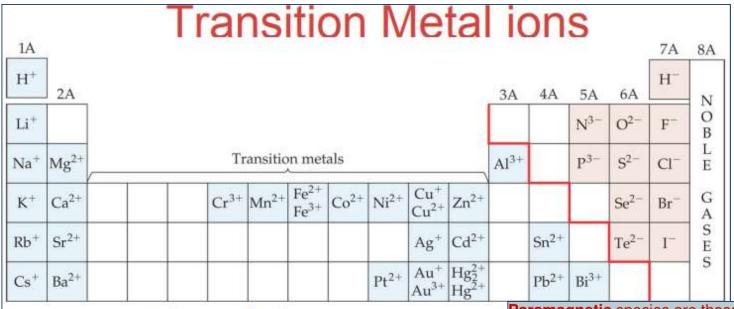
The inert pair effect leads to an increasing stability of an oxidation state that is 2 less than the group oxidation number for the heavier elements. d-Block elements exhibit a variety of oxidation states. The trends in stable oxidation states within the periodic table can be understood to some extent by considering electron configurations. Related factors such as ionization energies and spin correlation also play a role. 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.

A noble-gas configuration is achieved in the s and p blocks when eight electrons occupy the s and p subshells of the valence shell. In Groups 1, 2, and 13 the loss of electrons to leave the inner complete shell can be achieved with a relatively small input of energy. Thus, for these elements the oxidation numbers typical of the groups are 1, 2, and 3, respectively. From Group 14 to Group 17 it becomes increasingly energetically favourable—provided we consider the overall contributions to the energy, such as the interaction between oppositely charged ions—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 Code: SC202 Presented by elements already have a complete octet of electrons and are neither readily oxidized nor reduced.

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many have +2 charge

They actually lose all their ns electrons first

$$Mn --> Mn^{2+}$$
: [Ar]4s<sup>2</sup>3d<sup>5</sup> ---> [Ar]3d<sup>5</sup>

$$Cu --> Cu^+ [Ar]4s^23d^9 ---> [Ar]3d^{10}$$

Paramagnetic species are those that are attracted by a magnet (caused by unpaired electrons in an unfilled subshell)

<u>Diamagnetic</u> species are slightly repelled by magnets (caused by all electrons in subshell being paired)

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# Alkali Metals

- Found only as compounds in nature.
- · Have low densities and melting points.
- Also have low ionization energies.

Element	Electron Configuration	Melting Point (°C)	Density (g/cm <sup>3</sup> )	Atomic Radius (Å)	$I_1$ (kJ/mol)
Lithium	[He]2s <sup>1</sup>	181	0.53	1.34	520
Sodium	$[Ne]3s^1$	98	0.97	1.54	496
Potassium	$[Ar]4s^1$	63	0.86	1.96	419
Rubidium	$[Kr]5s^1$	39	1.53	2.11	403
Cesium	[Xe]6s <sup>1</sup>	28	1.88	2.25	376

# Alkaline Earth Metals

- Have higher densities and melting points than alkali metals.
- Have low ionization energies, but not as low as alkali metals.

Element	Electron Configuration	Melting Point (°C)	Density (g/cm <sup>3</sup> )	Atomic Radius (Å)	I <sub>1</sub> (kJ/mol)
Beryllium	[He]2s <sup>2</sup>	1287	1.85	0.90	899
Magnesium	$[Ne]3s^2$	650	1.74	1.30	738
Calcium	$[Ar]4s^2$	842	1.55	1.74	590
Strontium	[Kr]5s <sup>2</sup>	777	2.63	1.92	549
Barium	$[Xe]6s^2$	727	3.51	1.98	503

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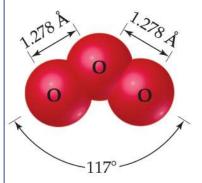
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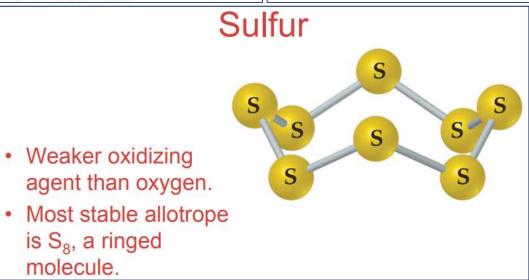
#### Group 6A Electron Melting Atomic I<sub>1</sub> (kJ/mol) Radius (Å) Element Configuration Point (°C) Density $[He]2s^22p^4$ 0.73 Oxygen -218 $1.43 \, g/L$ 1314 $[Ne]3s^23p^4$ $1.96 \, \text{g/cm}^3$ 1.02 Sulfur 15 1000 [Arl3d104s24p4 Selenium 221 $4.82 \text{ g/cm}^3$ 1.16 941 $[Kr]4d^{10}5s^25p^4$ 450 $6.24 \, \text{g/cm}^3$ 1.35 Tellurium 869 $[Xe]4f^{14}5d^{10}6s^26p^4$ Polonium 254 9.20 g/cm<sup>3</sup> 812

- Oxygen, sulfur, and selenium are nonmetals.
- Tellurium is a metalloid.
- The radioactive polonium is a metal.

# Oxygen



- Two allotropes:
  - > O2
  - > O<sub>3</sub>, ozone
- Three anions:
  - ➤ O<sup>2-</sup>, oxide
  - ► O<sub>2</sub><sup>2-</sup>, peroxide
  - ➤ O<sub>2</sub><sup>1-</sup>, superoxide
- Tends to take electrons from other elements (oxidation)



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# Group VIIA: Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	$I_1$ (kJ/mol)
Fluorine	$[He]2s^22p^5$	-220	1.69 g/L	0.71	1681
Chlorine	$[Ne]3s^23p^5$	-102	3.21 g/L	0.99	1251
Bromine	$[Ar]3d^{10}4s^24p^5$	-7.3	$3.12  \text{g/cm}^3$	1.14	1140
Iodine	$[Kr]4d^{10}5s^25p^5$	114	4.94 g/cm <sup>3</sup>	1.33	1008

# Group VIIIA: Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (Å)	I <sub>1</sub> (kJ/mol)
Helium	$1s^2$	4.2	0.18	0.32	2372
Neon	$[He]2s^22p^6$	27.1	0.90	0.69	2081
Argon	[Ne]3s <sup>2</sup> 3p <sup>6</sup>	87.3	1.78	0.97	1521
Krypton	$[Ar]3d^{10}4s^24p^6$	120	3.75	1.10	1351
Xenon	$[Kr]4d^{10}5s^25p^6$	165	5.90	1.30	1170
Radon	$[Xe]4f^{14}5d^{10}6s^26p^6$	211	9.73	1.45	1037

\*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

- Xe forms three compounds:
  - > XeF<sub>2</sub>
  - ➤ XeF<sub>4</sub> (at right)
  - ➤ XeF<sub>6</sub>
- Kr forms only one stable compound:
  - ► KrF<sub>2</sub>
- The unstable HArF was synthesized in 2000.

## Periodic characteristics of compounds

The number and type of bonds that elements form depend to a large extent on the relative strength of the bonds and the relative sizes of the atoms.

#### Coordination numbers

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

The coordination number of an atom in a compound depends very much on the relative sizes of the central atom and the surrounding atoms. 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  $NCl_3$  and four-coordinate ions such as  $NH_4$ , whereas its congener P forms molecules with coordination numbers of 3 and 5, as in  $PCl_3$  and  $PCl_5$ , and six-coordinate ionic species such as  $PCl_6$ . 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. However, it is more likely to be due to the possibility of arranging a greater number of atoms or molecules around the larger central atom. 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  $PCl_6$  ion whereas La forms the fluoride-bridged 9-coordinate  $PCl_6$  ion. Very high coordination numbers  $PCl_6$  fedience  $PCl_6$  in  $PCl_6$  in P

## Bond enthalpy trends

Bond enthalpies EH 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.

The mean bond enthalpy is the average bond dissociation enthalpy taken over a series of compounds. In the p block, EH 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.

Mean EX bond enthalpies for atoms that have lone pairs typically decrease down a group. However, the bond enthalpy for an element at the head of a group in Period 2 is anomalous and smaller than that of an element in Period 3:

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.

#### **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. The 3d metals form compounds with lower coordination numbers and oxidation states than the 4d and 5d elements. The oxidation state Ln(III) dominates in compounds of the lanthanoids, whereas the actinoids exhibit a variety of oxidation states.

The chemical properties of the first member of each group in the p block are significantly different from its congeners. These anomalies are attributable to the small atomic radius and its correlates, high ionization energies, high electronegativities, and low coordination numbers.

For example, in Group 14 carbon forms an enormous number of catenated hydrocarbons with strong CC bonds. Carbon also forms strong multiple bonds in the alkenes and alkynes. This tendency to catenation is much reduced for its congeners and the 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  $NF_3$ , and a coordination number of 4 in species such as  $NH_4$  and  $NF_4$  whereas phosphorus can form 3- and 5-coordinate compounds, such as  $PF_3$  and  $PF_5$ , and 6-coordinate species such as  $PF_6$ .

# Binary compounds

The simple binary compounds of the elements exhibit interesting trends in their structure and properties. Hydrogen, oxygen, and the halogens form compounds with most elements and the hydrides, oxides, and halides are reviewed here to give some insight into trends in bonding and properties.

# (a) Hydrides of the elements

Key point: The hydrides of the elements are classified as molecular, saline, or metallic. Hydrogen reacts with most elements to form hydrides that can be described as molecular, saline, or metallic, although some cannot be easily classified and are termed intermediate. Molecular compounds of hydrogen are common for the nonmetallic, electronegative elements of Groups 13 to 17; some examples are  $B_2H_6$ ,  $CH_4$ ,  $NH_3$ ,  $H_2O$ , and 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

Key point: Metals form basic oxides and nonmetals form acidic oxides. The elements form normal oxides, peroxides, superoxides, suboxides, and nonstoichiometric oxides.

The high reactivity of oxygen and its high electronegativity leads to a large number of binary oxygen compounds, many of which bring out high oxidation states in the second element.

*Metals typically form basic oxides.* 

Nonmetals form acidic oxides.

The acidic nature of the oxides increases across a row and decreases down a group for a given oxidation state. 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  $Tl_2O$ .

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# Halides of the elements

Key point: The s-block halides are predominantly ionic and the p-block halides are predominantly covalent. In the d block, low oxidation state halides tend to be ionic and high oxidation state halides tend to be covalent.

The halogens form compounds with most elements, but not always directly.

With the exception of Li and Be, the s-block halides are ionic and the p-block fluorides are predominantly covalent. Fluorine and Cl bring out the group oxidation number in most of the elements as well as an oxidation number 2 lower, as expected from the inert pair effect. Exceptions are N, O, and S, where only lower oxidation state halides are formed. 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 metal-metal bonds.