

Lecture 1; CH 101: Inorganic Chemistry

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Science & Chemistry

- ❖ Science – Derived from Latin “*Scientia*” which means to know
- ❖ Systematic undertaking that builds and/or organizes knowledge
- ❖ Rationalizes, explains and predicts based on observations
- ❖ Chemistry – Study of nature, properties and composition of matter and the associated changes
“Central Science” Organic, Inorganic, Physical

Inorganic Chemistry:

Understanding of the **physical** and chemical properties
of all inorganic compounds

Understand atoms to know about molecules

Origin of matter

Behavior of electrons in atoms

Atomic structure, ionization energy, electron affinity, electronegativity

Origin of Elements:

Occurrence of “Big Bang” about 1.5 billion years ago

Very high initial temperatures (Ca. 10^9 K)

Fundamental particles began to adhere together as the temperature cooled

1. Powerful attractive forces between nucleons
2. Weak but long-range electromagnetic force

Particle	Symbol	Mass	Mass number	Charge	Spin
Electron	e^-	5.486×10^{-4}	0	-1	1/2
Proton	p	1.0073	1	+1	1/2
Neutron	n	1.0087	1	0	1/2

Chemical Elements

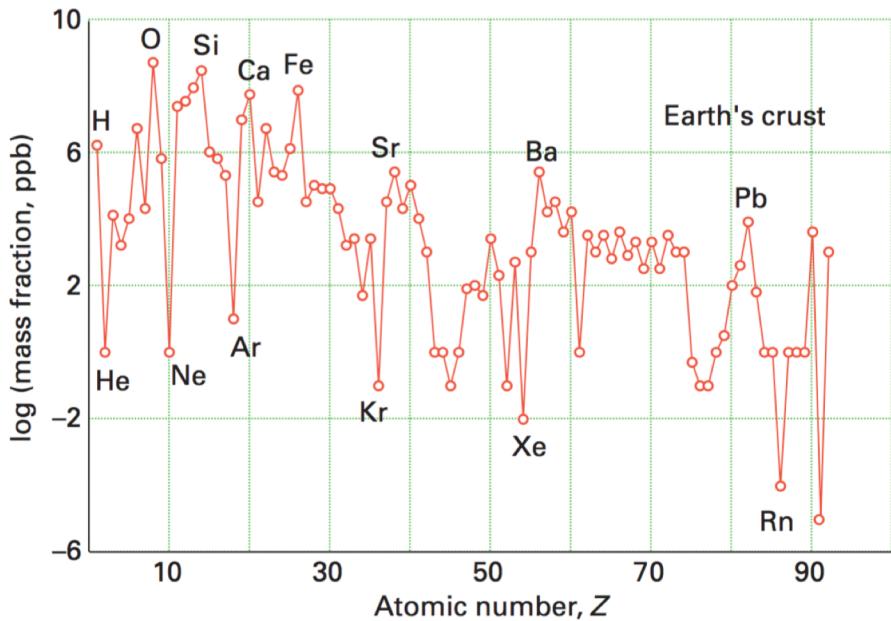
A total of 118 elements are known

94 elements occur naturally, 24 elements synthesized

Distinguished by their atomic number **Z**

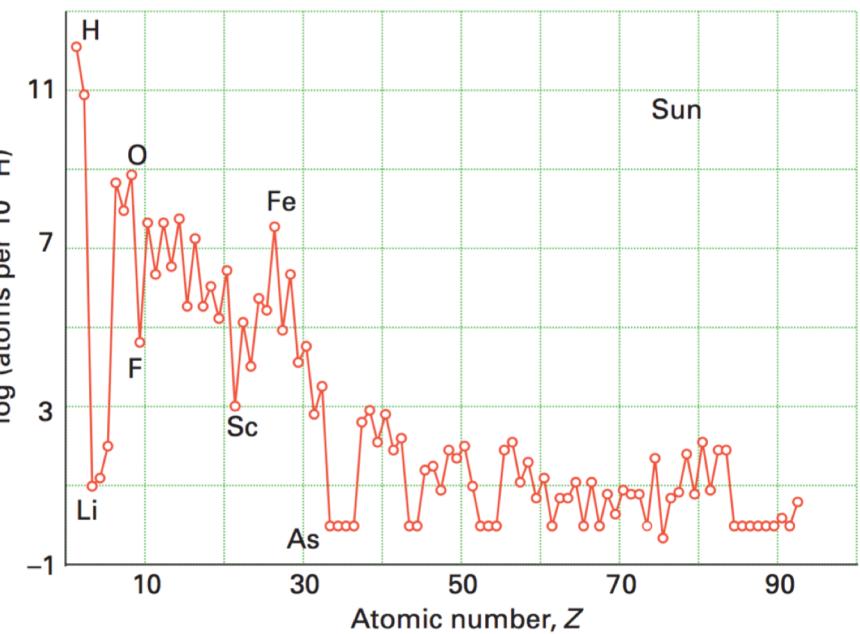
Many elements have isotopes which are atoms with same atomic number but with different atomic mass. Isotopes are distinguished by mass number **A**

Hydrogen ($Z = 1$) has 3 isotopes (${}^1\text{H}$, ${}^2\text{H}$, ${}^3\text{H}$)



The **abundances** of the elements in the Earth's crust and the Sun.

Elements with odd Z are **less stable** than their neighbours with even Z.



Structure of atoms

Consider hydrogen-like or hydrogenic atoms which have only one electron (H, He⁺, C⁵⁺)

Use the concept to describe structures of many-electron atoms

Spectroscopy: Electrons occupy certain energy levels and emission of discrete frequencies of electromagnetic radiation occurs when electron makes transition within these levels

Structure of atoms

Quantum Mechanics: Electrons can behave as particles or as waves

Schrodinger equation gives wave function which describes the location and properties of electrons in atom

The probability of finding an electron at a given location is proportional to square of the wavefunction

Wavefunctions have regions of positive and negative amplitude and can undergo constructive or destructive interference with one another

Atomic Orbitals

Wave function of an electron in an atom is called atomic orbital

Normally hydrogenic atomic orbitals are used to develop models that are central to the interpretation of inorganic chemistry

Each wavefunction obtained by solving Schrodinger equation is labelled by a set of three integers called quantum numbers n , l and m_l ,

Quantum Numbers

Principal quantum number n ; determines energy of the bound electron and indicates the size of the orbital

Orbital angular momentum quantum number l ; specifies the magnitude of orbital angular momentum and indicates the angular shape of the orbital with the number of lobes increasing as l increases

Magnetic quantum number m_l ; specifies the orientation of angular momentum (lobes)

Spin magnetic quantum number m_s ; anticlockwise (spin-up) with $m_s = +\frac{1}{2}$ and clockwise (spin-down, $m_s = -\frac{1}{2}$). NOTE: The fifth quantum number s is fixed at $\frac{1}{2}$

Shells, Subshells and Orbitals

All orbitals with a given value of n belong to the same shell. Shells with $n = 1, 2, 3, \dots$ are commonly referred to as K, L, M,..... shells

All orbitals of a given shell with the same value of l belong to the same subshell.

For a given value of n , the quantum number l can have values $l = 0, 1, \dots, (n-1)$

Value of $l = 0, 1, 2, 3, 4, \dots$

Subshell designation s, p, d, f, g

A subshell with quantum number l can have $2l+1$ orbitals which are distinguished by the value of m_l from $+l$ to $-l$

Atomic Orbitals

Regions where wavefunctions pass through zero are called nodes

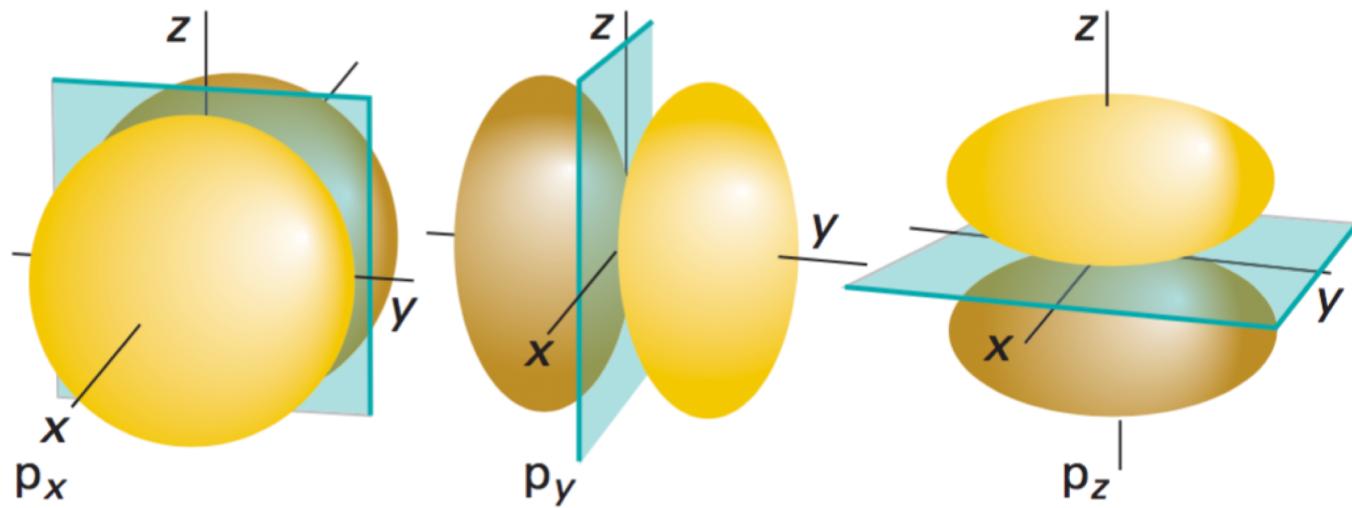
An orbital with quantum number n and l in general has $n - l - 1$ radial nodes

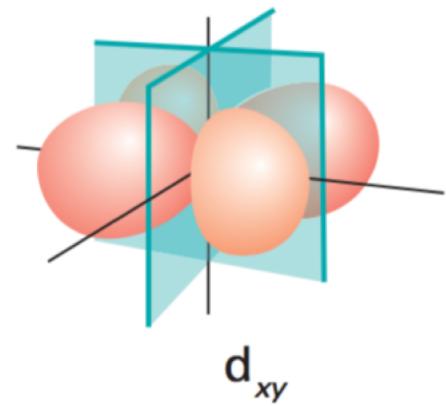
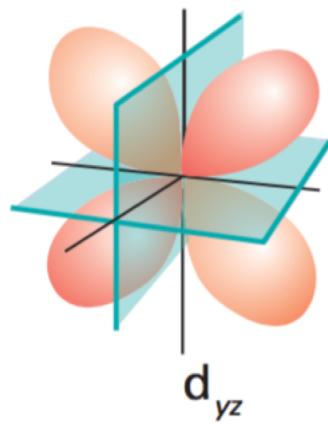
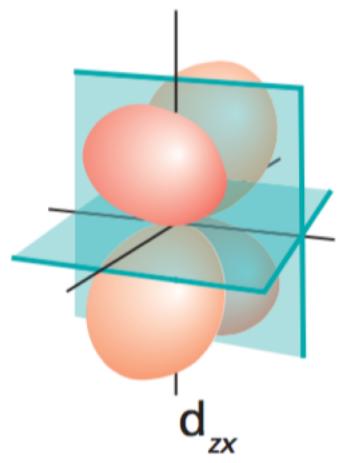
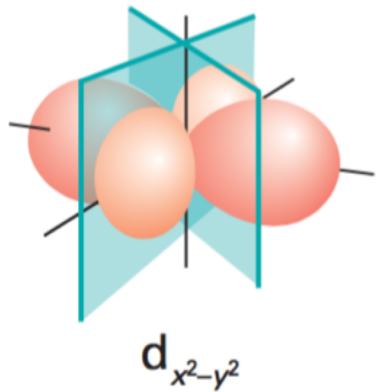
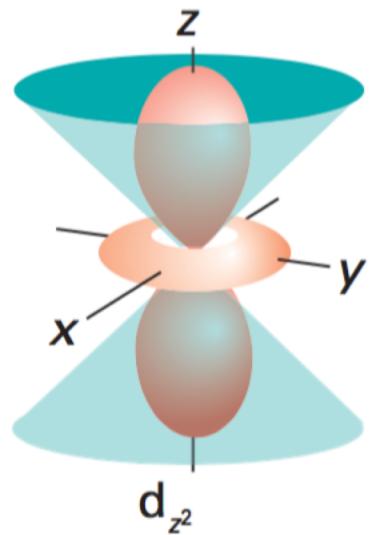
An s orbital has a non-zero amplitude at nucleus

All other orbital with $l > 0$ vanish at the nucleus

The boundary surface of an orbital indicates the region of space within which the electron is most likely to be found.

Orbital with quantum number l have l nodal planes





Penetration and Shielding:

Ground state electronic configuration: Specification of orbital occupation of an atom in its lowest energy state

Pauli's exclusion principle: Forbids occupancy of more than two electrons in the same orbital

The nuclear charge experienced by an electron is reduced by shielding by other electrons

$$Z_{\text{eff}} \text{ (effective)} = Z \text{ (True)} - \sigma \text{ (shielding constant)}$$

Order of energy levels in a shell of a many electron system s < p < d < f

Slater's Rules for the Determination of Effective Nuclear Charge (Z^*):

Depict the electronic configuration of the element while grouping the orbitals in the following order:

(1s)(2s, 2p)(3s, 3p)(3d)(4s, 4p)(4d)(4f)(5s, 5p).....

Sum up the following contributions to establish the screening constant for any electron:

1. Electrons in groups outside of the one being considered do not contribute to the shielding.
2. Electrons in the same group contribute 0.35 to the shielding (except the 1s group, where a contribution of 0.30 is used)

Slater's Rules for the Determination of Effective Nuclear Charge (Z^*):

3. If *s* or *p* electrons are being observed, each electron in the (n-1) shell contributes 0.85 to the shielding and each electron in the (n-2), (n-3), ... shells contribute 1.00 to the shielding
4. If the *d* or *f* electrons are being observed, each electron in underlying groups contributes 1.00 to the shielding.

Slater's Rules for the Determination of Effective Nuclear Charge (Z^*):

Electron configuration for Zn:

$$(1s)^2(2s, 2p)^8(3s, 3p)^8(3d)^10(4s)^2$$

$Z^* = Z - S$ (where Z = atomic number and S = screening constant)

$$\text{For a } 4s \text{ electron, } Z^* = 30 - (1 \times 0.35 + 18 \times 0.85 + 10 \times 1.00) = 30 - 25.65 = 4.35$$

$$\text{For a } 3d \text{ electron, } Z^* = 30 - (9 \times 0.35 + 18 \times 1.00) = 30 - 21.15 = 8.85$$

Building-Up:

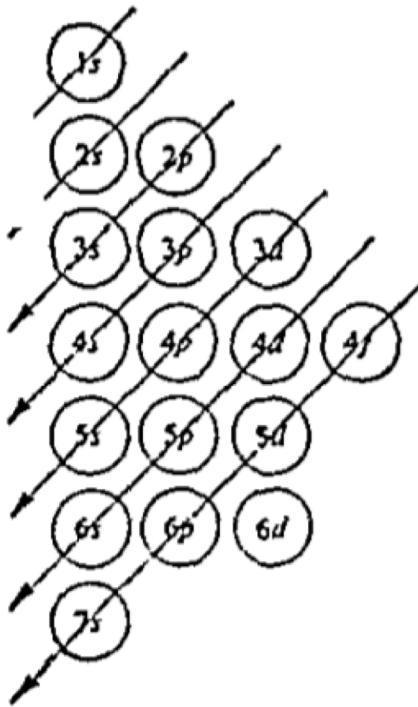
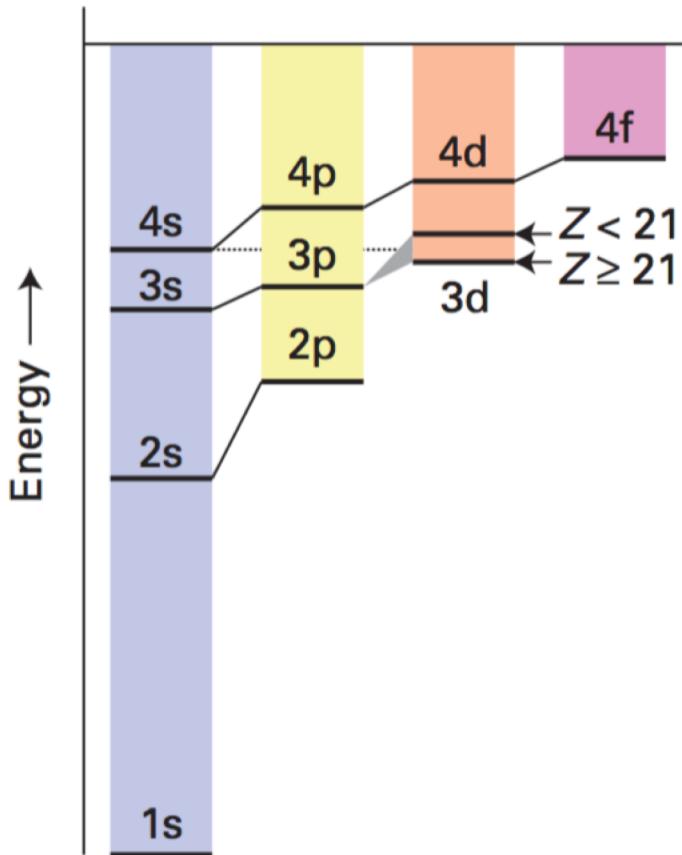


Figure 1.13 Sequence of filling energy levels

H	$1s^1$			
He	$1s^2$			
Li	$1s^2$	$2s^1$		
Be	$1s^2$	$2s^2$		
B	$1s^2$	$2s^2$	$2p^1$	
C	$1s^2$	$2s^2$	$2p^2$	
N	$1s^2$	$2s^2$	$2p^3$	
O	$1s^2$	$2s^2$	$2p^4$	
F	$1s^2$	$2s^2$	$2p^5$	
Ne	$1s^2$	$2s^2$	$2p^6$	
Na	$1s^2$	$2s^2$	$2p^6$	$3s^1$

The Building-Up Principle

The order of occupation of atomic orbitals

$1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, \dots$

Degenerate orbitals are occupied singly before being doubly occupied

Certain deviations occur in occupancy for d and f orbitals

For elements with incompletely filled d subshell
 $d^n s^2$ (despite 3d orbitals being lower in energy)

For corresponding cations and complexes, the configuration is always d^n

The Building-Up Principle

Cr: [Ar]3d⁵s¹ rather than [Ar]3d⁴s²

Cu: [Ar]3d¹⁰4s¹ rather than [Ar]3d⁹4s²

Pd: [Ar]4d¹⁰5s⁰ rather than [Ar]4d⁸5s²

Gd: [Xe]4f⁷5d¹6s² rather than [Xe]4f⁸5d⁰6s²

Fe: [Ar]3d⁶4s² whereas for Fe(CO)₅ [Ar]3d⁸

Similarly for Fe²⁺: [Ar]3d⁶

Classification of Elements

Metals, Non-metals and Metalloids in accordance with their physical and chemical properties

Widely accepted organization of elements –
Mendeleev's periodic table

Metals: lustrous, malleable, ductile, electrically conducting (**Fe, Cu**)

Non-metals: gases (**oxygen**), liquids (**bromine**) and solids (**sulphur**) that do not conduct electricity.

Metalloids: Elements having properties that make it difficult to classify either as metals or as non-metals (**Si, Ge, As, Te**)

Bonding:

Why do atoms form bonds? A molecule will be formed only if it is more **stable** is lower in energy than individual atoms

Group 18 elements (noble gases) are generally **monoatomic**. Atoms already have low energy (associated with their having a **complete outer shell of electrons**)

Only **electrons in outermost shell** participate in bonding and by forming bonds each atom attains a **stable electron configuration**.

Bonding: Types

Atoms can attain stable electron configuration by losing, gaining or sharing electrons

Ionic bonds are formed when there is a complete transfer of one or more electrons from one atom to another (between metals & non-metals, resulting compounds are typically hard & non-volatile)

Covalent bonding involves the sharing of a pair of electrons between two atoms (between non-metals, resulting compounds are typically volatile)

In metallic bonds, the valence electrons are free to move throughout the whole crystal (results in alloys)

Periodic Table:

Organizing principle that coordinates and rationalizes the diverse physical and chemical properties (which are usually governed by number of electrons in the outer shell and their arrangement) of elements.

Elements are arranged in the order of increasing atomic number (atomic mass)

Each element has one more orbital electron than the preceding element

Elements arranged in several horizontal rows (**periods**) in the periodic table such that each row begins with an **alkali metal** and ends with an **noble gas**

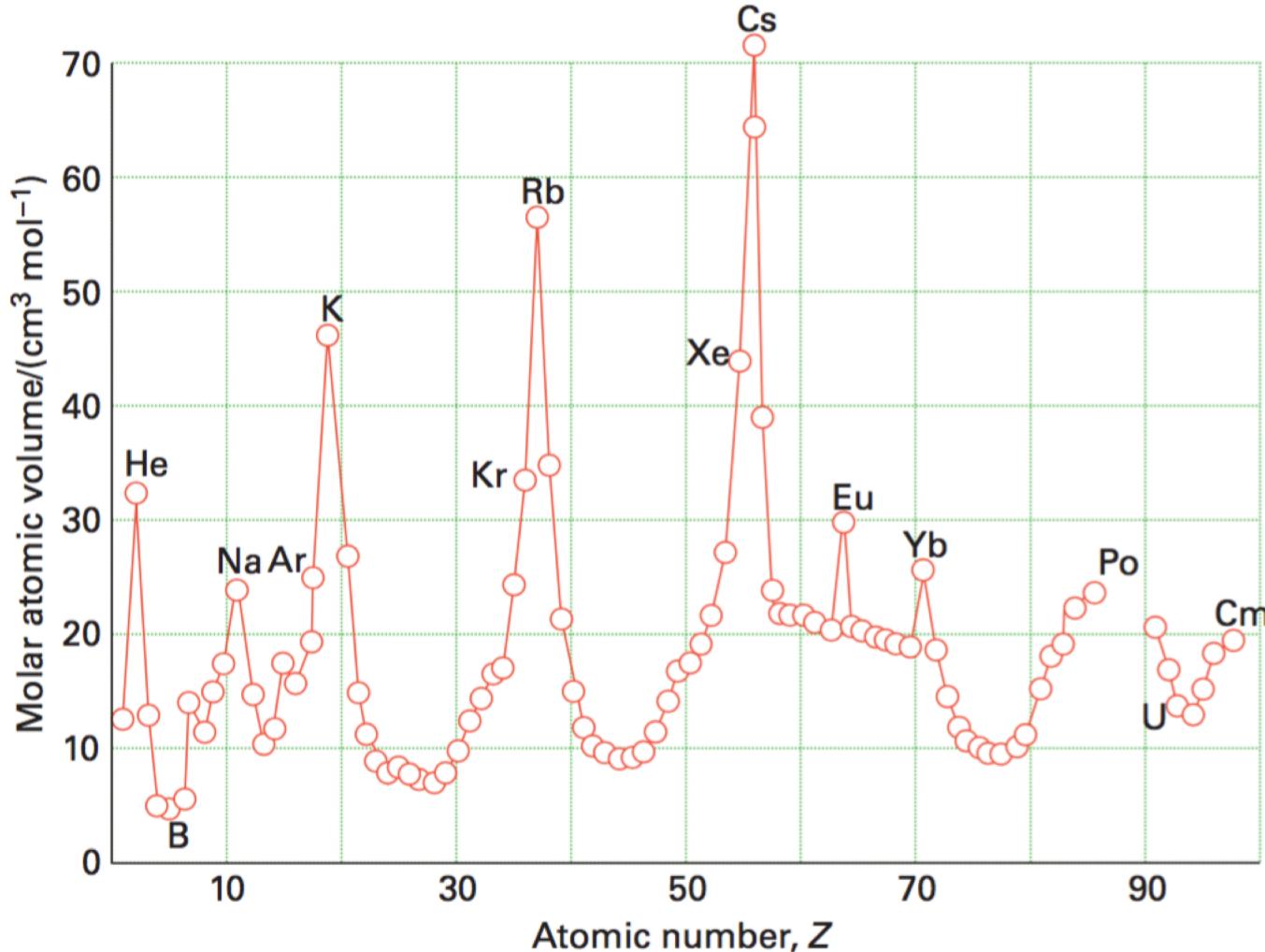
Periodic Variations

A group has elements with similar outer electronic configuration

Mendeleev's arrangement resulted in elements within a group shows similarities in chemical properties (C, Si, Ge and Sn all form hydrides of the general formula EH_4 . Similarly, N, P, As and Sb form hydrides of the general formula EH_3)

Lothar Meyer found that elements within a period shows similarities in physical properties

Periodic Variations



Periodic variation of molar volume with atomic number

Periodic Table: *Format*

Blocks of the periodic table reflect the identity of the orbitals that are occupied last in the building up process

The period number is the principal quantum number of the valence shell

The group number is related to the number of valence electrons

Block	s	p	d
Valence electrons	G	G-10	G

Periodic Table: *s*-Block Elements

Properties result from the presence of *s* electrons.

Group 1 (alkali metals): Elements with one *s* electron in their outer shell

Group 2 (alkaline earth metals): Elements with two *s* electrons in their outer shell

Periodic Table: *p*-Block Elements

Properties dependent on the presence of *p* electrons.

Group 13 : Elements with three electrons (two s and one *p*) in their outer shell

Group 14 :Elements with four electrons (two s and two *p*) in their outer shell

Similarly, Group 15 (two s and three *p* electrons), Group 16 (two s and four *p* electrons), Group 17 (two s and five *p* electrons) and Group 18 (two s and three *p* electrons) belong to the *p*-block elements

Periodic Table: *d*-Block Elements

Elements where *d* orbitals are being filled are called *d*-block or transition elements

d electrons are being added to the penultimate shell

Group 3 : Elements with one *d* electron in the penultimate shell

Group 4 :Elements with two *d* electrons in the penultimate shell

Up to ten *d* electrons can be added; hence transition metals are arranged in group 3 to group 12

Periodic Table: *f*-Block Elements

Elements where *f* orbitals are filled are called *f*-block elements

In this case the *f* electrons enter the antepenultimate shell

Periodic Table: Atomic and Ionic Radii

Atomic radius: Half the internuclear distance between neighboring atoms

Metals: Metallic radius;

Non Metals: Covalent radius

Ionic radius: Distance between centres of neighboring anions and cations

Periodic Table: Atomic Radii

Atomic radii increase down a group and decrease from left to right across a period

On descending the group, valence electrons are added to orbitals of successively higher principal quantum number

Across a period, the valence electrons enter the orbitals of the same shell

Any deviations ?

Periodic Table: Atomic Radii - Deviations

Deviations from the expected trend occurs between elements within a group of the third row and second row d-block elements due to lanthanide contraction

Li	Be											B	C	N	O	F
157	112											88	77	74	73	71
Na	Mg											Al	Si	P	S	Cl
191	160											143	118	110	104	99
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
235	197	164	147	135	129	137	126	125	125	128	137	140	122	122	117	114
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
250	215	182	160	147	140	135	134	134	137	144	152	150	140	141	135	133
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
272	224	188	159	147	141	137	135	136	139	144	155	155	154	152		

Periodic Table of Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																																																				
1 H Hydrogen 1.00794	2 He Helium 4.002602	3 Li Lithium 6.941	4 Be Beryllium 9.012182	5 Na Sodium 22.98976928	6 Mg Magnesium 24.3050	7 Alkali metals	8 Alkaline earth metals	9 Lanthanoids	10 Transition metals	11 Poor metals	12 Other nonmetals	13 Noble gases	14 Metals	15 Nonmetals	16 K Potassium 39.0983	17 Ar Argon 39.948	18 Kr Krypton 83.798																																																				
1 C Solid	2 Hg Liquid	3 H Gas	4 Rf Unknown	5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797	11 S Sulfur 32.065	12 P Phosphorus 30.973762	13 Se Selenium 78.96	14 Br Bromine 79.904	15 As Arsenic 74.92180	16 Se Selenium 78.96	17 Kr Krypton 83.798	18 Xe Xenon 131.293	19 Zr Zirconium 91.224																																																			
20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.887	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.548	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92180	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Tl Thallium 118.710	51 Sn Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.50447	54 Xe Xenon 131.293	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57-71 89-103	72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.9866569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (208.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)	87 Fr Francium (223)	88 Ra Radium (226)	104 Rf Rutherfordium (281)	105 Db Dubnium (282)	106 Sg Seaborgium (286)	107 Bh Bohrium (284)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium (294)	118 Uuo Ununoctium (294)
57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.984	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92353	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9686	72 Ac Actinium (227)	73 Th Thorium 232.03606	74 Pa Protactinium 231.03588	75 U Uranium 238.02691	76 Np Neptunium (237)	77 Pu Plutonium (244)	78 Am Americium (243)	79 Cm Curium (247)	80 Bk Berkelium (247)	81 Cf Californium (251)	82 Es Einsteinium (252)	83 Fm Fermium (257)	84 Md Mendelevium (258)	85 No Nobelium (259)	86 Lr Lawrencium (262)																																								

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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Periodic Table: Atomic Radii - Deviations

Elements in the third row of *d*-block are preceded by elements of first row of *f*-block (lanthanoids)

Poor shielding of *f*-orbitals results in valence electrons being more attracted to nucleus than expected

The repulsion between electrons being added across the *f*-block fail to compensate for the increasing Z_{eff}

Net result: Decrease in atomic radii as one goes from La to Lu

Similar effect is found in elements that follow *d*-block

Periodic Table: Ionic Radii

Variation in ionic radii through the periodic table similar to that of atomic radii

All monoatomic anions are larger than their parent atoms

Greater electron-electron repulsions

Decrease in Z_{eff}

Similarly, all monoatomic cations are smaller than their parent atoms

Reduced electron-electron repulsions

Increase in Z_{eff}

Why is there a large increase in ionic radius on going from Si^{4+} (42 pm) to P^{3-} (198 pm) ion?

Answer: Si^{4+} has an electron arrangement of $1s^2\ 2s^2\ 2p^6$, i. e. two occupied energy levels. P^{3-} has an electron arrangement of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, i. e. three occupied energy levels. The third energy level is further from the nucleus. As a result, the atomic radius of P^{3-} is higher than Si^{4+} .

Why Cl^- (181 pm) is smaller than P^{3-} (212 pm) ion?

Answer: Both Cl^- and P^{3-} ions have the same electronic configuration. However, the Cl^- has 17 protons in its nucleus, while P^{3-} has only 15. The chloride is smaller because its electrons are drawn closer to the higher positive charge on its nucleus, as force of attraction F is proportional to Z .

Periodic Table: Ionization Energy

Minimum energy required to remove an electron from a gas-phase atom

First ionization energy: Energy required to remove the least tightly bound electron from neutral atom

Second ionization energy: Energy required to remove the least tightly bound electron from resulting cation

Periodic Table: Ionization Energy

Largely determined by highest occupied orbital

$$I = E(A^+, g) - E(A, g)$$

First ionization energy varies systematically and follows the pattern of effective nuclear charge Z_{eff}
 $I \propto Z_{\text{eff}}^2/n^2$

First ionization energy is the smallest at lower left (near Cs) and greatest near the upper right (near He)

Elements with small atomic radii have high ionization energies and *vice versa*

I (kJ/mol) Deviations

H								He
1312								2373
								5259
Li	Be	B	C	N	O	F		Ne
513	899	801	1086	1402	1314	1681		2080
7297	1757	2426	2352	2855	3386	3375		3952
11809	14844	3660	4619	4577	5300	6050		6122
		25018						
Na	Mg	Al	Si	P	S	Cl		Ar
495	737	577	786	1011	1000	1251		1520
4562	1476	1816	1577	1903	2251	2296		2665
6911	7732	2744	3231	2911	3361	3826		3928
		11574						
K	Ca	Ga	Ge	As	Se	Br		Kr
419	589	579	762	947	941	1139		1351
3051	1145	1979	1537	1798	2044	2103		3314
4410	4910	2963	3302	2734	2974	3500		3565
Rb	Sr	In	Sn	Sb	Te	I		Xe
403	549	558	708	834	869	1008		1170
2632	1064	1821	1412	1794	1795	1846		2045
3900	4210	2704	2943	2443	2698	3197		3097
Cs	Ba	Tl	Pb	Bi	Po	At		Rn
375	502	590	716	704	812	926		1036
2420	965	1971	1450	1610	1800	1600		
3400	3619	2878	3080	2466	2700	2900		

Periodic Table: Successive Ionization

Successive ionizations of an element require increasingly higher energies

Higher the positive charge, greater is the electrostatic attraction experienced by the electron being removed

Removal of successive electrons increases Z_{eff} and as a result the atom contracts

TRENDS ARE NEVER SIMPLE

Arrange the following elements in increasing order of first ionization energy.

Na, Mg, Al, Si, P, S, Cl

Answer: Na ($3s^1$) < Al ($3s^2 3p^1$) < Mg ($3s^2$) < Si ($3s^2 3p^2$) < S ($3s^2 3p^4$) < P ($3s^2 3p^3$) < Cl ($3s^2 3p^5$)

The valence electron configurations of the elements are given within the brackets.

Ionization potential increases from left to right across a period. The discrepancies of Mg/Al and P/S pairs can be explained in terms of higher stability of completely filled and half-filled s and p orbitals.

Periodic Table: Electron Affinity

Change in energy when a gaseous atom gains electron

May be exothermic or endothermic $E_a = E(A, g) - E(A^-, g)$

Largely determined by lowest unfilled orbital

A positive (high) electron affinity indicates that the ion A has a lower, more negative energy than the neutral atom, A. 2nd electron addition is invariably endothermic

An element has a high electron affinity, if the additional electron experiences a strong Z_{eff}

Elements close to F (but not inert gases) have high electron affinity. (N_2 is an Exception!!)

N	O	F	$E_a / (\text{kJ mol}^{-1})$
-8	141	328	

Periodic Table: Electronegativity

Tendency of an element to attract electrons to itself when it is part of a compound.

$$\chi_M = \frac{1}{2}(I + E_a)$$

$$\chi_P = 1.35\chi_M^{1/2} - 1.37$$

$$\chi_{AR} = 0.744 + \frac{35.90Z_{eff}}{(r / pm)^2}$$

It is useful to

Rationalize bond energies

Predict the type of reactions

Prediction of polarities of bonds and molecules

Periodic Table: Electronegativity

Electronegativity of an element is high if the two frontier orbitals of its atoms are low in energy

In general there is an increase in electronegativity across a period

Elements with high Z_{eff} and small covalent radius have high electronegativity

Electronegativity decreases down a group

Periodic Table: Polarizability

Ability to be distorted by an electric field

Polarizability likely to be high if the separation of frontier orbitals is **small** (typically found for large, heavy atoms and ions)

Polarizability will be low if the separation of frontier orbitals is **large**

Ability of species to distort the electron distribution of neighboring atoms – **Polarizing ability**

Periodic Table: Polarizability; Fajan's Rules

Small, highly charged cations have polarizing ability

Large, highly charged anions are easily polarized

Cations that do not have noble gas configuration are easily polarized.

Arrange the diatomic halogen molecules in increasing order of their boiling points. Give suitable explanations for your answer.

Answer: The order of boiling points of halogens is $F_2 < Cl_2 < Br_2 < I_2$

Explanation: In this case, the bonding is primarily covalent in nature. The boiling point depends on the degree of intermolecular forces holding the molecules together in the liquid state. Because the strength of a London dispersion force increases with the polarizability of the element's electron cloud and the polarizability in turn depends on the diffuseness (or size) of the atom, the boiling points of the halogens increase with increasing atomic radius.