Lecture 2; CH 101: Inorganic Chemistry

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Penentration 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_{eff} (effective) = Z (True) - σ (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:
(1*s*)(2*s*, 2*p*)(3*s*, 3*p*)(3*d*)(4*s*, 4*p*)(4*d*)(4*f*)(5*s*, 5*p*)........

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:

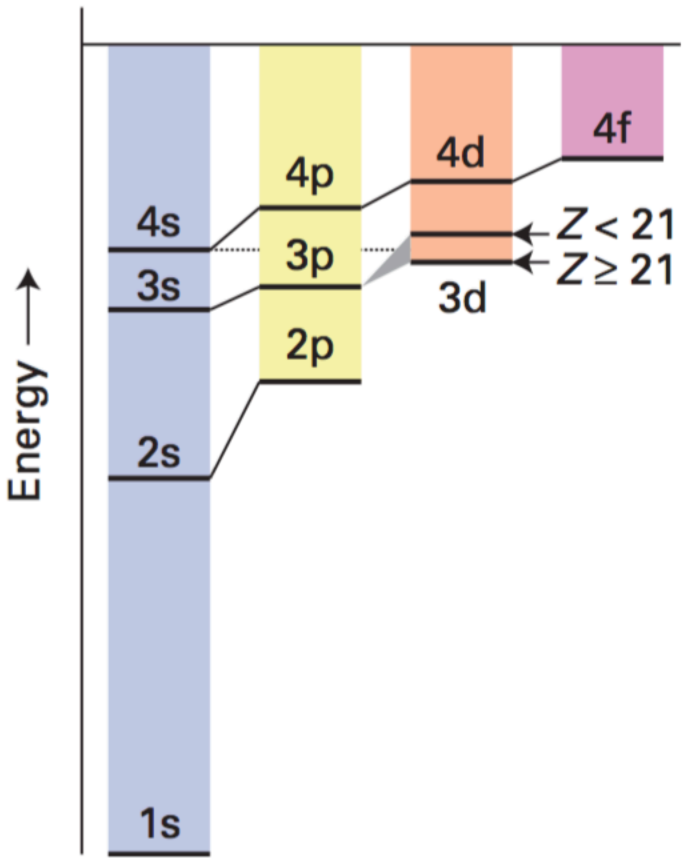
$(1s)^2(2s, 2p)^8(3s, 3p)^8(3d)^{10}(4s)^2$

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

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

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

Building-Up:



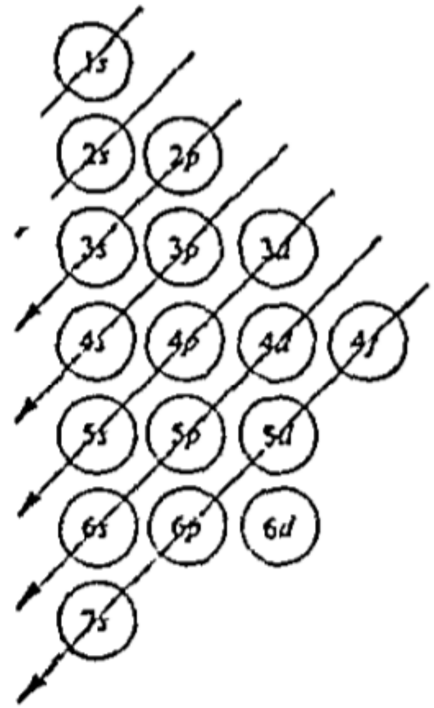


Figure 1 13 Sequence of filling energy levels

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

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*,…

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: $[Ar]3d^5s^1$ rather than $[Ar]3d^4s^2$

Cu: $[Ar]3d^{10}4s^1$ rather than $[Ar]3d^94s^2$

Pd: $[Ar]4d^{10}5s^0$ rather than $[Ar]4d^85s^2$

Gd: $[Xe]4f^75d^16s^2$ rather than $[Xe]4f^85d^06s^2$

Fe: $[Ar]3d^64s^2$ whereas for $Fe(CO)_5$ $[Ar]3d^8$

Similarly for Fe^{2+}:$[Ar]3d^6$

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

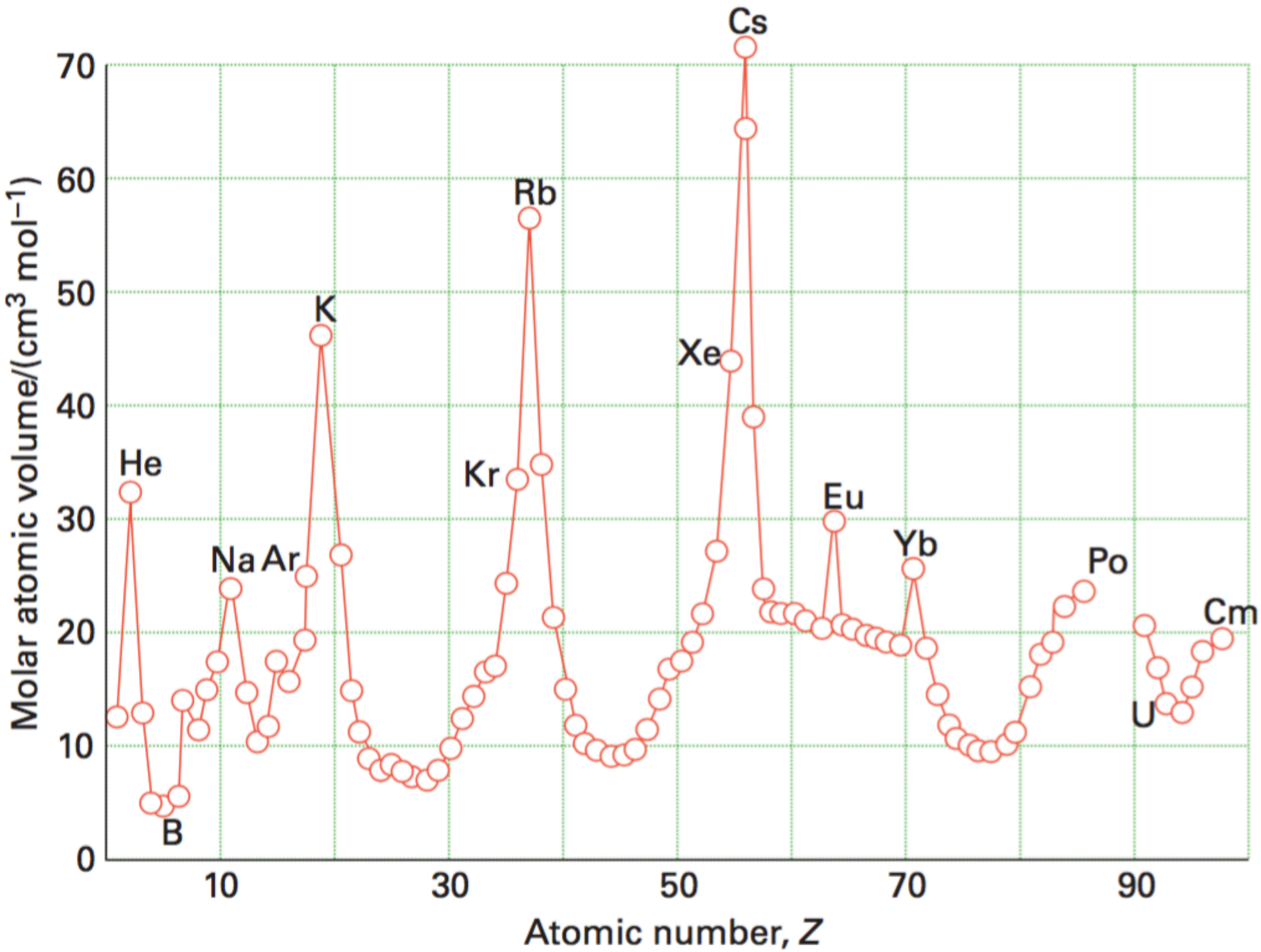
Periodic Variations

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