

Lecture 3; CH 101: Inorganic Chemistry

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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	Atomic # Symbol Name Atomic Mass																2 He Helium 4.002602	
<div><div>C Solid</div><div>Hg Liquid</div><div>H Gas</div><div>Rf Unknown</div></div>																		
<div><div>Metals</div><div>Alkali metals</div><div>Alkaline earth metals</div><div>Lanthanoids</div><div>Actinoids</div><div>Transition metals</div><div>Poor metals</div><div>Other nonmetals</div><div>Noble gases</div></div>																		
3 Li Lithium 6.941	4 Be Beryllium 9.012182											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 Na Sodium 22.98976928	12 Mg Magnesium 24.3050											13 Al Aluminium 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948	
19 K Potassium 39.0983	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 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798	
37 Rb Rubidium 85.468	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 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293	
55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57–71										80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209.9824)	85 At Astatine (209.9871)	86 Rn Radon (222.0176)
87 Fr Francium (223)	88 Ra Radium (226)	89–103										112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (292)	117 Uus Ununseptium	118 Uuo Ununoctium (294)

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

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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 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	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 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03588	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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 an high electron affinity, if the additional electron experiences a strong Z_{eff}

Elements close to F (but not inert gases) have high electron affinity. (N₂ 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.

$$\chi_{\text{M}} = \frac{1}{2}(I + E_{\text{a}})$$

$$\chi_{\text{P}} = 1.35\chi_{\text{M}}^{1/2} - 1.37$$

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

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.