

1.6. Review of Electronegativity (χ)

CONCEPT: Electronegativity is a very useful concept for the explanation or understanding of chemical reactivity throughout the periodic table.

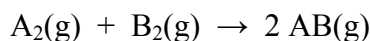
- There are many definitions of electronegativity. The resulting numerical values are not interchangeable.
- Original definition by Linus Pauling:

“the power of an atom in a molecule to attract electrons to itself”

- Pauling noticed that the bond energies of polar bonds (A-B) were greater than the average of the bond energies of the two homonuclear species (avg. A-A & B-B).
(RECALL: the strength of the *siloxane* linkage -Si-O-Si-O-)

Pauling Definition:

Derives values for electronegativity χ_P by comparing bond energies:



$$\begin{aligned}\Delta E_{(AB)} &= E_{(AB)\text{exp}} - \frac{1}{2}(E_{(AA)} + E_{(BB)}) \\ &= 23 (\chi_A - \chi_B)^2 \text{ [kcal/mol]} \quad \text{excess energy from ionic contribution}\end{aligned}$$

$$|\chi_A - \chi_B| = 0.208 \Delta E^{1/2} \text{ [eV]}$$

$$|\chi_A - \chi_B| = \text{bond polarity}$$

Set $\chi_F = 3.98$ and $\chi_H = 2.2$, then calculate all other values using experimental data. (See p.31 of your text for actual values.)

Mulliken Definition: Derives values for (“absolute”) electronegativity χ_M from ionization energy and electron affinity.

$$\chi_M = \frac{1}{2} (IE + EA) = -\mu \quad \text{NOTE: this is the average of IE and EA}$$

IE = ionization energy of an atom, EA = Electron Affinity of an atom, μ = chemical potential of the electrons.

- Pauling and Mulliken scales are very much in line. One reasonably accurate conversion between the two is:

$$\chi_{\text{Pauling}} = 1.35(\chi_{\text{Mulliken}})^{1/2} - 1.37$$

Allred + Rochow Definition:

Describes χ_A electronegativity as “a force” needed to remove an electron from the atom’s ground state. (Note the similarity to Coulomb’s Law).

$$\chi_A = 0.359 \frac{Z^*_A}{r_A^2} + 0.744$$

Z^*_A = effective nuclear charge from Slater’s rules

r_A = atomic radius of A (from A-A) in Å

NOTE: The larger the effective nuclear charge (Z^*), the more electronegative.

- This implies that electronegativity is different for each orbital of an atom and is dependent on electron filling (i.e., charge).

NOTE: The smaller the atomic radius, the more electronegative.

Allen Definition:

“Electronegativity is the *average* one-electron energy of the valence-shell electrons in ground-state free atoms.”

i.e., VOIP – Valence Orbital Ionization Potential

Spectroscopic electronegativity:

$$\chi_{spec} = \frac{m\epsilon_p + n\epsilon_s}{m + n}$$

m, n = number of p and s electrons, respectively

ϵ_s, ϵ_p = multiplet averaged ionization potentials of p and s electrons (experimental data).

e.g., Consider a carbon atom: C is $[\text{He}]2s^22p^2$ valence shell is $n = 2$

There are 15 possible ways of filling 2 electrons into the three p orbitals: 15 microstates

Some of these microstates have the same energy as each other, some have different energies. So the *average* energy is:

$$\bar{E}_{GS} = \frac{1}{15} \{E(^1S) + 5E(^1D) + 9E(^3P)\}$$

“Electronegativity is the 3rd dimension of the periodic table.”

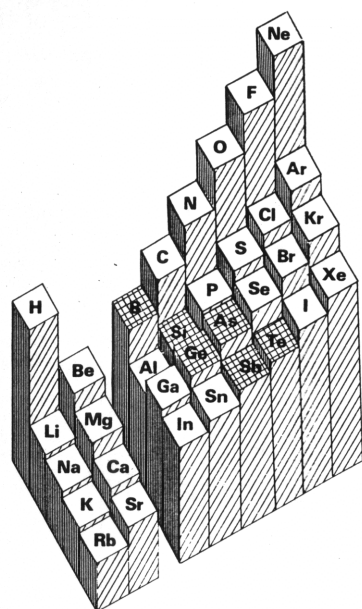


Figure 1. Electronegativity, $\chi_{\text{spec}} = (m\epsilon_p + n\epsilon_s)/(m + n)$, where m , ϵ_p , n , ϵ_s are the number and ionization potentials (multiplet averaged) of p and s electrons in the valence shell of representative elements through the 5th row. ϵ_p and ϵ_s were obtained from National Bureau of Standards high-resolution atomic energy level tables (ref 1). Cross-hatched atoms are those of the metalloid band.

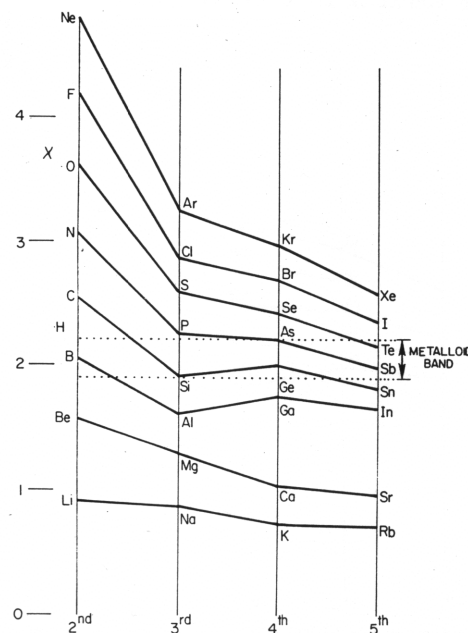


Figure 2. χ_{spec} from experimental atomic energy level data versus rows. Family of curves for groups I–VIII of the representative elements. Pauling units (scale set by equating χ_{spec} average of Ge and As to combined average of Allred & Rochow and Pauling scale Ge and As values). Metalloid band has Si as the lower limit and As as the upper limit.

Source: L.C. Allen, J. Am. Chem. Soc., 1989, **111**, 9003-9014

- The “metalloids” are the elements roughly along the diagonal from B to Po.
- Some metalloids have both metallic and non-metallic *allotropes*.

Note the general trends:

1. Elements with $n = 2$ valence orbitals are significantly more electronegative than the other elements in their respective groups.
2. Hydrogen has approx. same electronegativity as carbon.
3. Noble gases are the most electronegative elements in their period.
4. EN decreases down a group, except: **B > Al < Ga** and **C > Si < Ge**
This is called the **alternation effect**.
Increased nuclear charge accompanies filling of the 3d orbitals. The 3d electrons shield the **4p** electrons poorly, making Ga and Ge more electronegative.

Consider again: $C(s^2p^2)$

- Energy of the groundstate is given by the average of the energy of each microstate (cf. multiplet averaged energies in **Allen's definition**)

$$\bar{E}_{GS} = \frac{1}{15} \{E(^1S) + 5E(^1D) + 9E(^3P)\}$$

- Can do the same for $C^+(s^2p)$ and $C^-(s^2p^3)$
- The resulting Mulliken electronegativity is in fact the electronegativity of the p-orbital of the C-atom!
- What are the electronegativities of $(sp)p^2$, $(sp^2)p$, and sp^3 hybridized carbons?

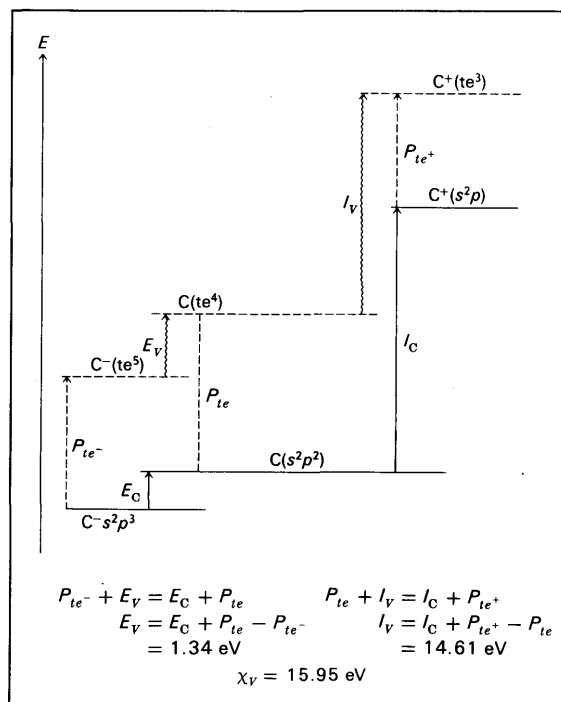


Figure 1-20. Diagram of the relationships between average configuration energy, valence state energy, and promotion, ionization, and electron affinity energies.

Source: Purcell & Kotz, Inorganic Chemistry, 1977

→ need to know the valence state promotion energies to calculate the orbital electronegativities.

- These energies can be calculated (see Hinze et al., JACS, **85**, (1963), 148, and Hinze & Jaffe, J. Phys. Chem., **67**, (1963), 1501.)

Comparison between the various scales:

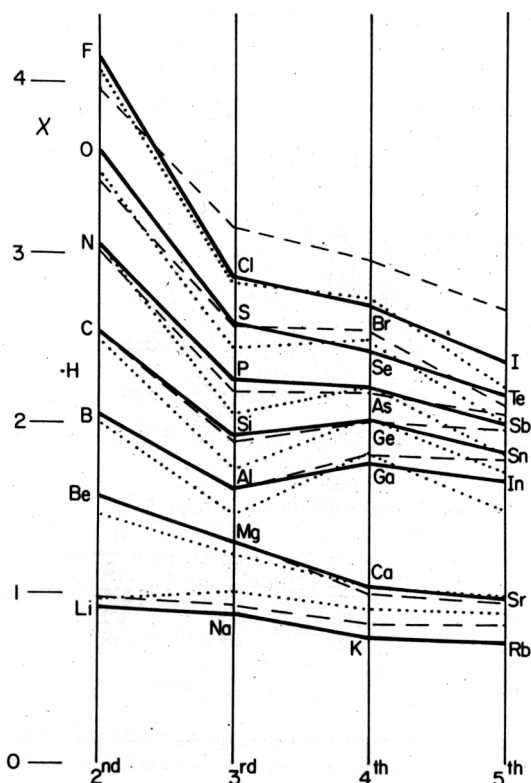


Figure 3. χ_{spec} , experimental values (solid lines), compared to Pauling scale (dashed lines) and to Allred & Rochow scale (dotted lines).

KEY TREND: Within the main group elements, electronegativity increases from left to right across a period and decreases down a group.

Orbital electronegativities:

- Since atomic EN values depend on ionization potentials of individual electrons,

EN = f(actual electron configuration) as expressed by the appropriate term symbol:

$$\text{IP}(2s^2 2p^2) \neq \text{IP}(2s^1 2p^3)$$

i.e., the EN depends on which orbital an electron is removed from!

→ *orbital electronegativity*

The results:

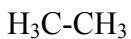
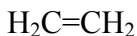
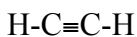
TABLE 1-5
SOME MULLIKEN ELECTRONEGATIVITIES (eV)

H									
s	7.2								
Li	Be	B	C	N	O	F			
s 3.1	di ² 4.8	tr ³ 6.4	di ² π^2 10.4, 5.7	di ³ π^2 15.7, 7.9	tr ⁵ π 17.1, 20.2	s 31.3			
p 1.8	te ² 3.9	te ³ 6.0	tr ³ π 8.8, 5.6	tr ⁴ π 12.9, 8.0	di ² π^4 19.1	p 12.2			
			te ⁴ 8.0	te ⁵ 11.6	te ⁶ 15.3				
Na	Mg	Al	Si	P	S	Cl			
s 2.9	di ² 4.1	tr ³ 5.5	di ² π^2 9.0, 5.7	di ³ π^2 11.3, 6.7	tr ⁴ π^2 10.9	s 19.3			
p 1.6	te ² 3.3	te ³ 5.4	tr ³ π 7.9, 5.6	tr ⁴ π 9.7, 6.7	te ⁶ 10.2	p 9.4			
			te ⁴ 7.3	te ⁵ 8.9					
K	Ca	Ga	Ge	As	Se	Br			
s 2.9	di ² 3.4	tr ³ 6.0	di ² π^2 9.8, 6.5	di ³ π^2 9.0, 6.5	tr ⁴ π^2 10.6	s 18.3			
p 1.8	te ² 2.5	te ³ 6.6	tr ³ π 8.7, 6.4	tr ⁴ π 8.6, 7.0	te ⁶ 9.8	p 8.4			
			te ⁴ 8.0	te ⁵ 8.3					
Rb	Sr	In	Sn	Sb	Te	I			
s 2.1	di ² 3.2	tr ³ 5.3	di ² π^2 9.4, 6.5	di ³ π^2 9.8, 6.3	tr ⁴ π^2 10.5	s 15.7			
p 2.2	te ² 2.2	te ³ 5.1	tr ³ π 8.4, 6.5	tr ⁴ π 9.0, 6.7	te ⁶ 9.7	p 8.1			
				te ⁵ 8.5					

Values can be computed only for orbitals holding 1 electron. For the carbon and nitrogen families it is possible to have both hybrid and π atomic orbitals half-filled. *digonal* \equiv sp hybrid, *trigonal* \equiv sp^2 hybrid, *tetrahedral* \equiv sp^3 hybrid.

Source: Purcell & Kotz, Inorganic Chemistry, 1977

Which is the most acidic?



Take home message:

The electronegativity of an atom is (in part) a function of its environment!

1.7 Hardness: “Absolute hardness is the resistance of the chemical potential to change the number of electrons”

... in other words: The harder a chemical species, the more difficult it will be to change its oxidation state.

Pearson and Parr have derived the following definition for “hardness” η .

$$\eta = \frac{1}{2}(\text{IE} - \text{EA})$$

Q. How does this differ from Mulliken’s definition of electronegativity?

Lit.: R.G. Parr, R.G. Pearson, *JACS*, **105**, (1983), 7512-7516.

Absolute electronegativity χ :

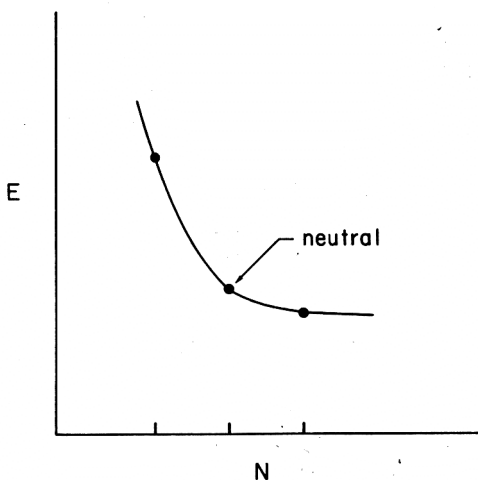


Figure 1.

$$\chi = -\left(\frac{\partial E}{\partial N}\right) \approx -\frac{\Delta E}{\Delta N} = -\frac{(-EA - IP)}{1 - (-1)} = \frac{(IP + EA)}{2} = -\mu$$

μ = chemical potential of the electrons

Absolute hardness η :

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right) = \frac{1}{2} (IP - EA)$$

$$2\eta = \left(\frac{\partial \mu}{\partial N} \right) = - \left(\frac{\partial \chi}{\partial N} \right)$$

Absolute softness σ :

$$\sigma = 1/\eta$$

Koopman's theorem (recall from CHEM 206):

$$E_{\text{HOMO}} \approx -IP$$

$$E_{\text{LUMO}} \approx -EA$$

From these definitions:

The larger the energy gap $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, the harder the chemical species.

Note: Always $IP \geq EA$ for a neutral species

Minimum hardness is = 0; maximum softness (achieved for bulk metals: $\sigma \rightarrow \infty$)

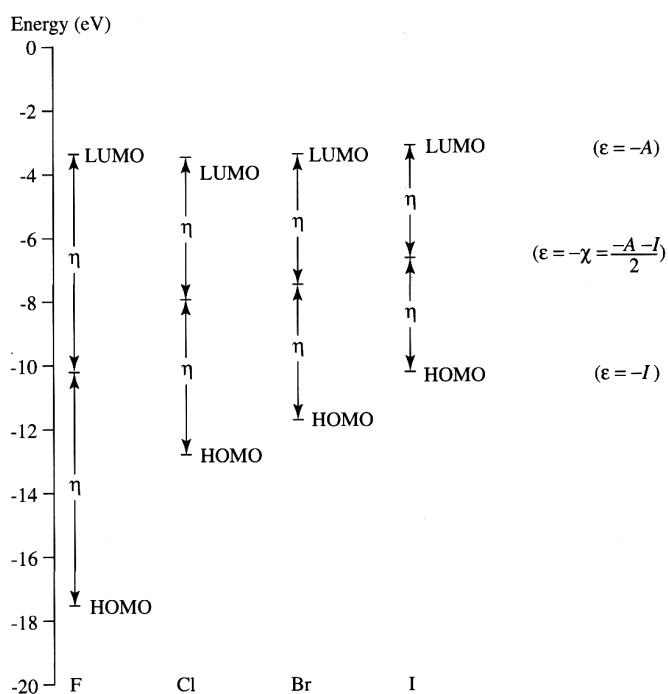


FIGURE 6-8 Energy Levels for Halogens. Relation between absolute electronegativity (χ), absolute hardness (η), and HOMO and LUMO energies for the halogens.

Source: Tarr & Miessler, Inorganic Chemistry, Prentice-Hall, 1998:

1.8 Polarizability

- Polarizability α is an atom's ability to be distorted by an electric field (such as that of a neighboring ion).
- Atoms (and ions) are highly polarizable if their electron distribution can be distorted readily.
- High polarizability is most likely to occur when unfilled atomic orbitals lie close in energy to the highest occupied atomic orbital(s), i.e., when there is a small energy difference between highest occupied and lowest unoccupied orbitals.
- Closely separated frontier orbitals are typically found for large, heavy atoms and ions, whereas small, light atoms typically have widely spaced energy levels.

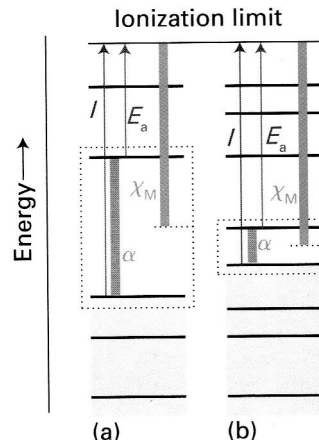


Fig. 1.28 The interpretation of the electronegativity and polarizability of an element in terms of the energies of the frontier orbitals (the highest filled and lowest unfilled atomic orbitals). (a) Low electronegativity and polarizability; (b) high electronegativity and polarizability.

Fajan's rules

1. Small, highly charged cations are able to polarize other atoms (high polarizing ability).
2. Large, highly charged anions are easily polarized.
3. Cations that do not have a noble-gas electron configuration are easily polarized (note that this refers in particular to transition metals, see CHEM365)

1.9 Atomic and ionic radii

Atomic radius – half the internuclear distance between neighboring atoms of the same element in a metal (metallic radius) or in a molecule (covalent radius).

Ionic radius – typically determined by assigning the radius of O^{2-} (in an O_h hole of a solid oxide crystal) as 1.40 Å and subsequently determining other ionic radii from experimental data.

KEY TREND: Atomic radii increase down a group. Within the main group atomic radii decrease from left to right across a period.

Table 1.5. Metallic radii (in Å)*

Li	Be														
1.57	1.12														
Na	Mg												Al		
1.91	1.60												1.43		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga			
2.35	1.97	1.64	1.47	1.35	1.29	1.27	1.26	1.25	1.25	1.28	1.37	1.53			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn		
2.50	2.15	1.82	1.60	1.47	1.40	1.35	1.34	1.34	1.37	1.44	1.52	1.67	1.58		
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	
2.72	2.24	1.72	1.59	1.47	1.41	1.37	1.35	1.36	1.39	1.44	1.55	1.71	1.75	1.82	

* The values refer to coordination number 12 (see Section 4.3). Source: A. F. Wells, *Structural inorganic chemistry*, 5th edn. Clarendon Press, Oxford (1984).

Table 1.6. Ionic radii (in Å)*

Li ⁺ (4) 0.59	Be ²⁺ (4) 0.27	B ³⁺ (4) 0.12	C	N ³⁻ 1.71	O ²⁻ (6) 1.40	F ⁻ (6) 1.33
Na ⁺ (6) 1.02	Mg ²⁺ (6) 0.72	Al ³⁺ (6) 0.53	Si	P ³⁻ 2.12	S ²⁻ (6) 1.84	Cl ⁻ (6) 1.81
K ⁺ (6) 1.38	Ca ²⁺ (6) 1.00	Ga ³⁺ (6) 0.62	Ge	As ³⁻ 2.22	Se ²⁻ (6) 1.98	Br ⁻ (6) 1.96
Rb ⁺ (6) 1.49	Sr ²⁺ (6) 1.16	In ³⁺ (6) 0.79	Sn	Sb ³⁻	Te ²⁻ (6) 2.21	I ⁻ (6) 2.20
Cs ⁺ (6) 1.70	Ba ²⁺ (6) 1.36	Tl ³⁺ (6) 0.88	Pb	Bi ³⁻	Po ²⁻	At ⁻

* Numbers in parentheses are the coordination numbers of the ions. Values for ions without a coordination number stated are estimates.

Source: R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, **B25**, 925 (1969).

“Inorganic Chemistry, 2nd Ed.” Shriver, Atkins and Langford, W. H. Freeman and Co., N.Y., 1990.

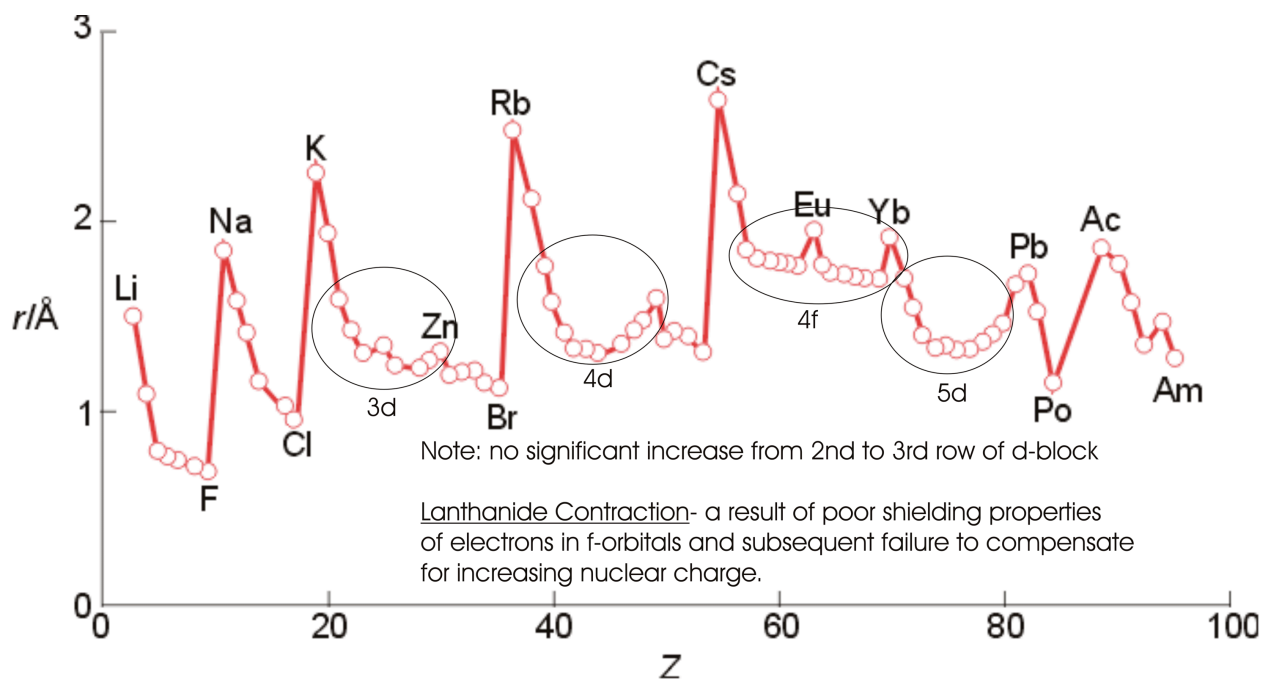
NOTE: O^{2-} ionic radius is arbitrarily set at 1.40 Å; all others are derived from this.

Question: Why is O^{2-} an obvious choice as a reference ion for radius measurements?

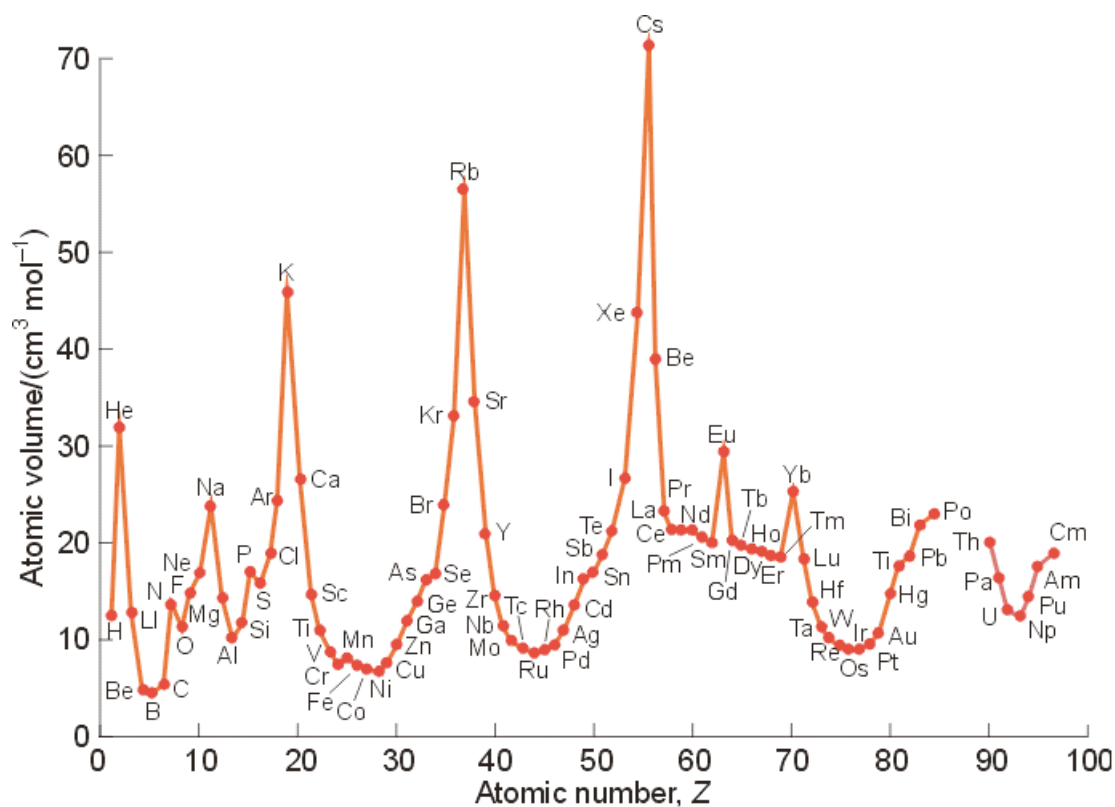
Suggested readings: Chapter 9 Note that this is a chapter on periodic trends in general. Much of the content is cross-referenced elsewhere in the textbook.

See your textbook for a table of atomic radii, p.23.

Atomic Radii:



Atomic Volume:



Source: Shriver & Atkins, Inorganic Chemistry, 3rd Edition, Freeman 1999