Topic 1F - Periodicity

Periodic Properties of the Elements

Periodic Trends

Effective nuclear charge (Z_{eff})
Atomic radii
Ionization energy
Electron affinity
Electronegativity

Uniqueness Principle

Small size of second-row atoms
Increased likelihood of π-bonding
Lack of d-orbitals

Diagonal Relationships

Ionic size
Charge density
Electronegativity

Inert-Pair Effect

Ionization energies
nd and nf electrons not effective shields

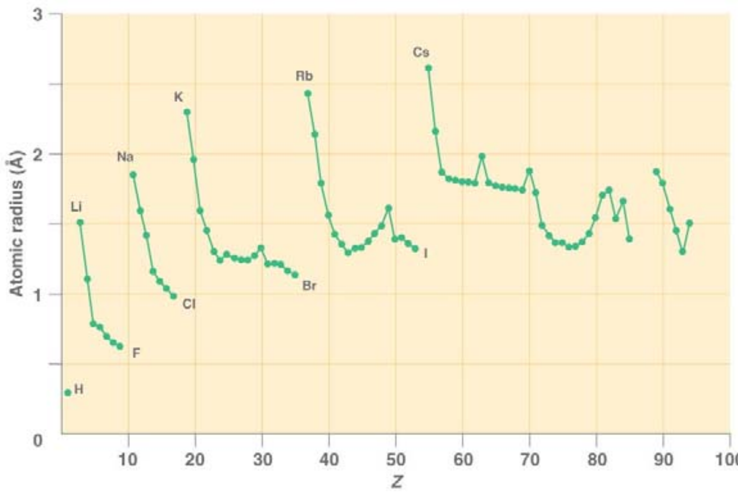
Element Types

Metals
Non-metals
Metalloids

TABLE 10.1
Effective Nuclear Charges for Selected Atoms

	H(1)							He(2)
1s	1.00							1.69
	Li (3)	**Be(4)**	**B (5)**	**C (6)**	**N(7)**	**O(8)**	**F(9)**	**Ne(10)**
1s	2.69	3.68	4.68	5.67	6.66	7.66	8.65	9.64
2s	1.28	1.91	2.58	3.22	3.85	4.49	5.13	5.76
2p			2.42	3.14	3.83	4.45	5.10	5.76

Periodic Variations in Atomic Radii:



1 H 0.30																	2 He —
3 Li 1.52	4 Be 1.11											5 B 0.80	6 C 0.77	7 N 0.70	8 O 0.66	9 F 0.64	10 Ne —
11 Na 1.86	12 Mg 1.60											13 Al 1.43	14 Si 1.17	15 P 1.10	16 S 1.04	17 Cl 0.99	18 Ar —
19 K 2.31	20 Ca 1.97	21 Sc 1.60	22 Ti 1.46	23 V 1.31	24 Cr 1.25	25 Mn 1.29	26 Fe 1.26	27 Co 1.25	28 Ni 1.25	29 Cu 1.28	30 Zn 1.33	31 Ga 1.22	32 Ge 1.22	33 As 1.21	34 Se 1.17	35 Br 1.15	36 Kr —
37 Rb 2.44	38 Sr 2.15	39 Y 1.80	40 Zr 1.57	41 Nb 1.43	42 Mo 1.36	43 Tc 1.3	44 Ru 1.33	45 Rh 1.34	46 Pd 1.38	47 Ag 1.44	48 Cd 1.49	49 In 1.62	50 Sn 1.40	51 Sb 1.41	52 Te 1.37	53 I 1.33	54 Xe —
55 Cs 2.62	56 Ba 2.17	57 La 1.88	72 Hf 1.50	73 Ta 1.43	74 W 1.37	75 Re 1.37	76 Os 1.34	77 Ir 1.35	78 Pt 1.38	79 Au 1.44	80 Hg 1.55	81 Tl 1.71	82 Pb 1.75	83 Bi 1.55	84 Po 1.67	85 At 1.4	86 Rn —

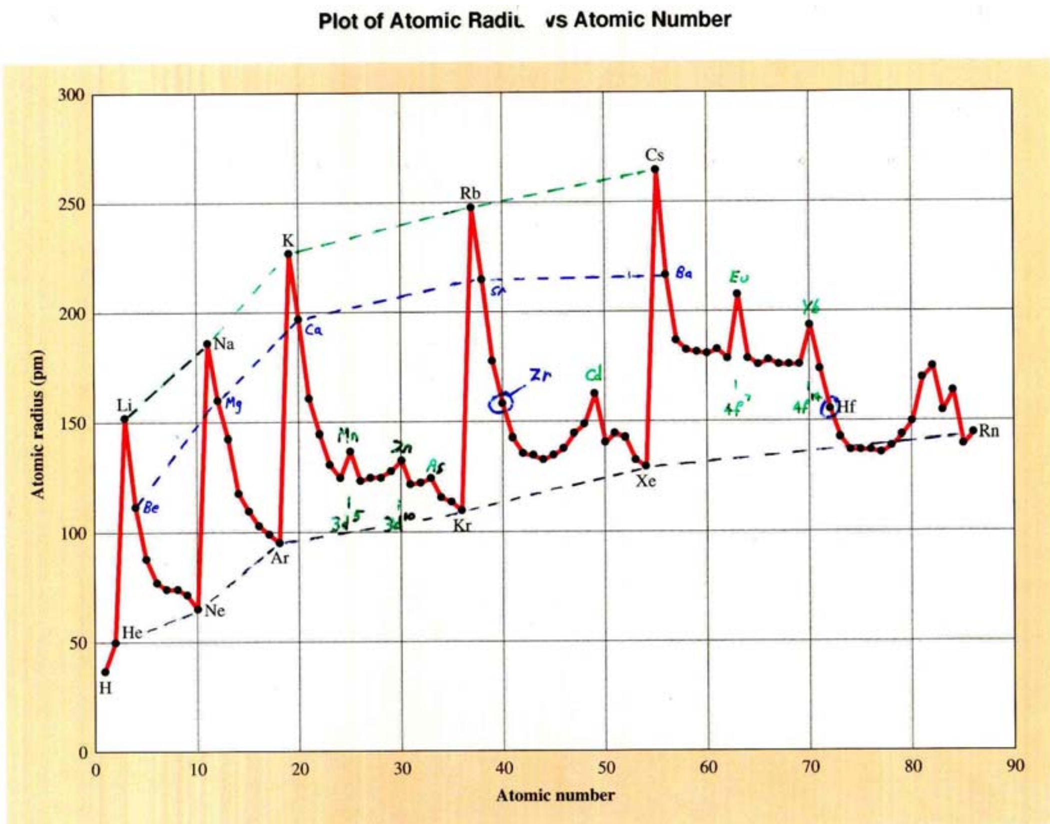
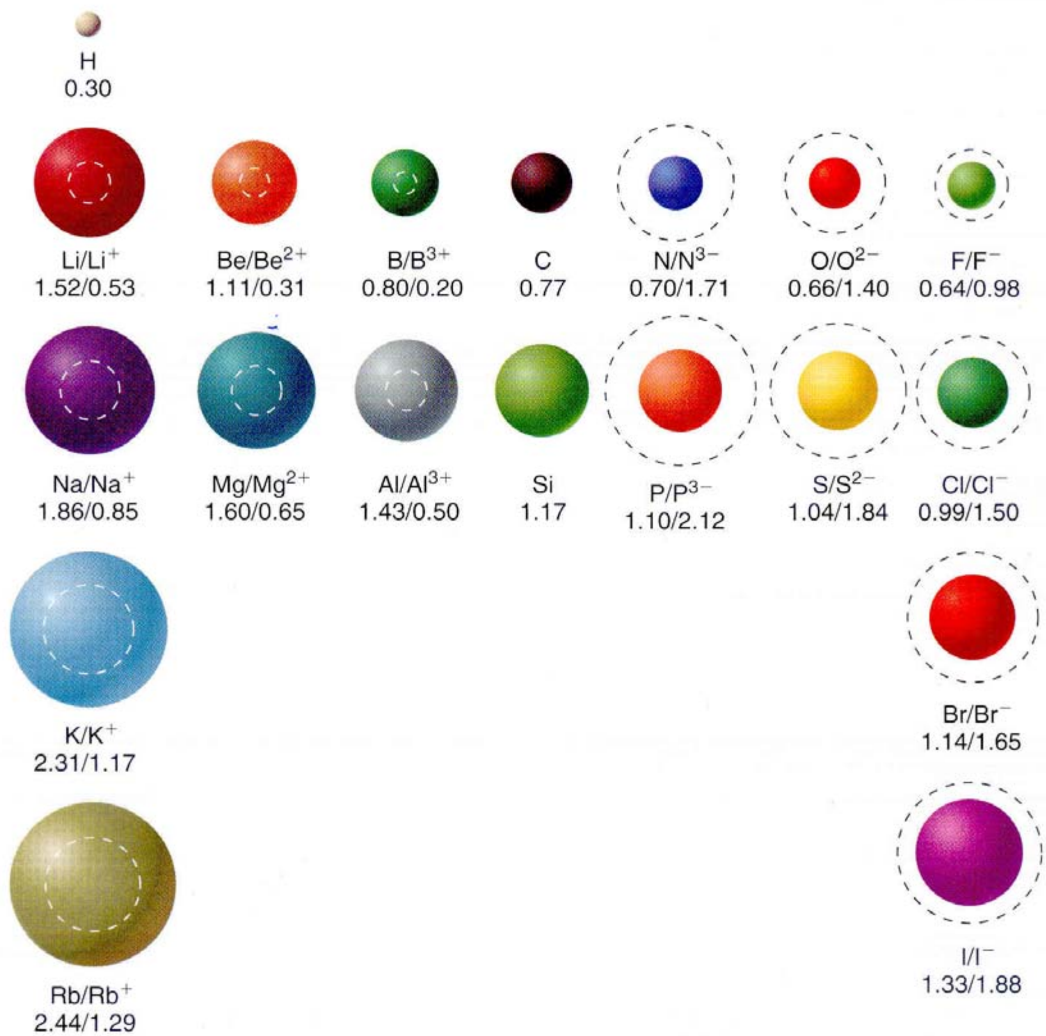
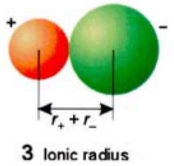

Plot of Atomic Radius vs Atomic Number
Atomic radius (pm)
Atomic number
0
50
100
150
200
250
300
0
10
20
30
40
50
60
70
80
90
H
He
Li
Be
Ne
Na
Mg
Ar
K
Ca
Mn
Zn
As
Kr
Rb
Sr
Zr
Cd
Xe
Cs
Ba
Eu
Yb
Hf
Rn

Figure 4.13: Atomic and Ionic Sizes



Radii of ions

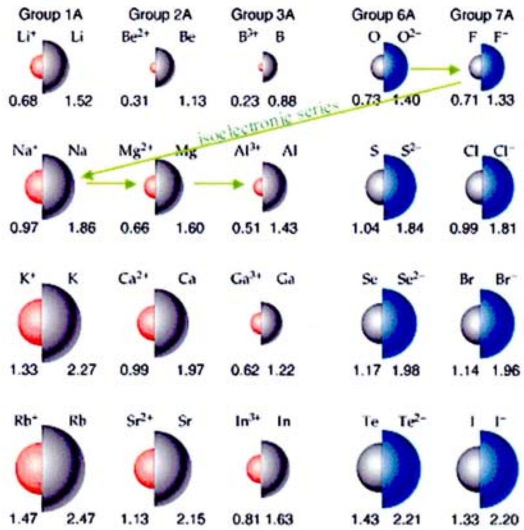


This is a "self-consistent" scale based on O^{-2} = 1.40 (or 1.38) Å.

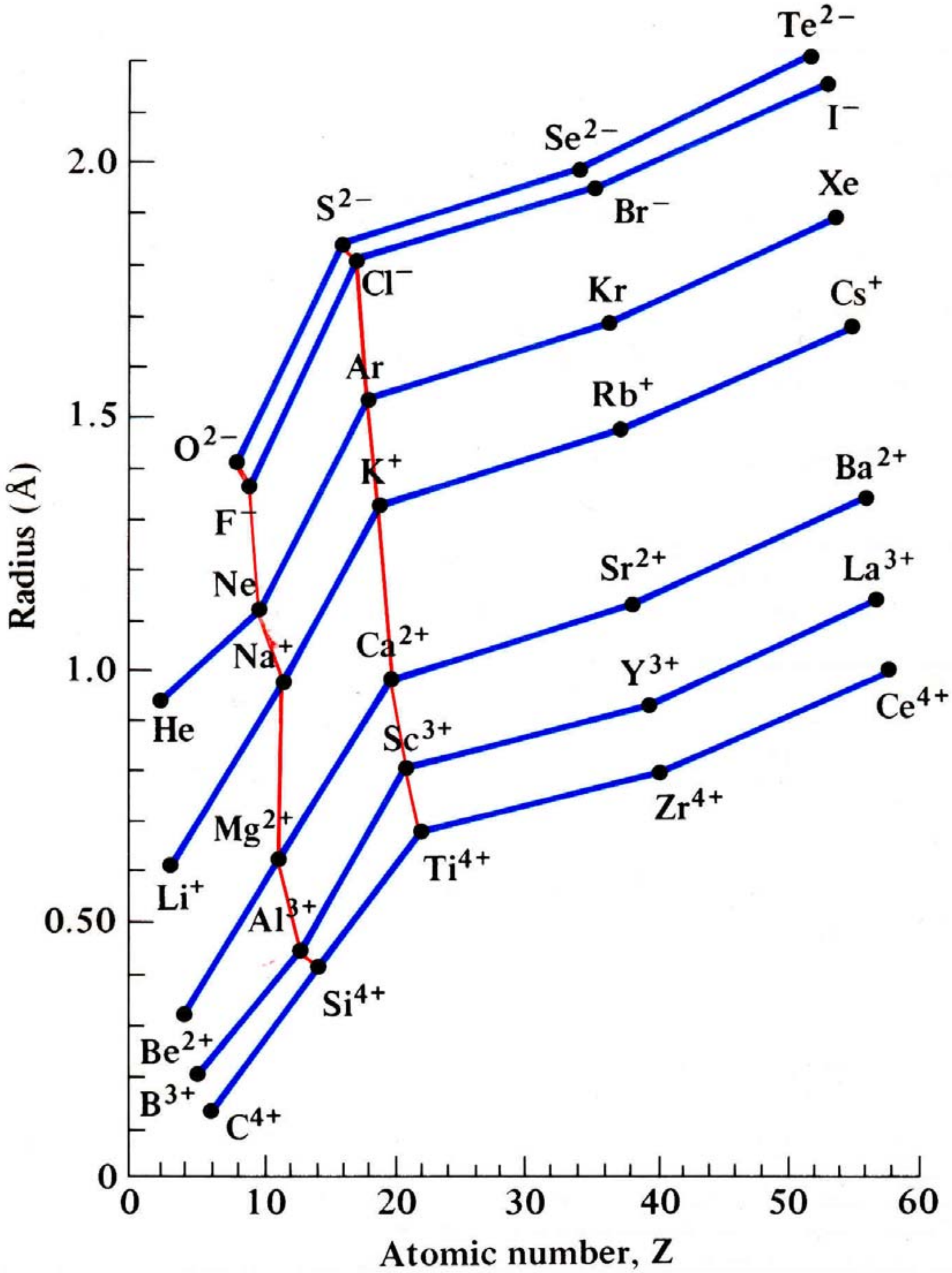
Ionic radii depend on the magnitude of the charge of the ion and its environment.

Positively charged ions are smaller than their neutral analogues because of increased *Z**.

Negatively charged ions are larger than their neutral analogues because of decreased *Z**.

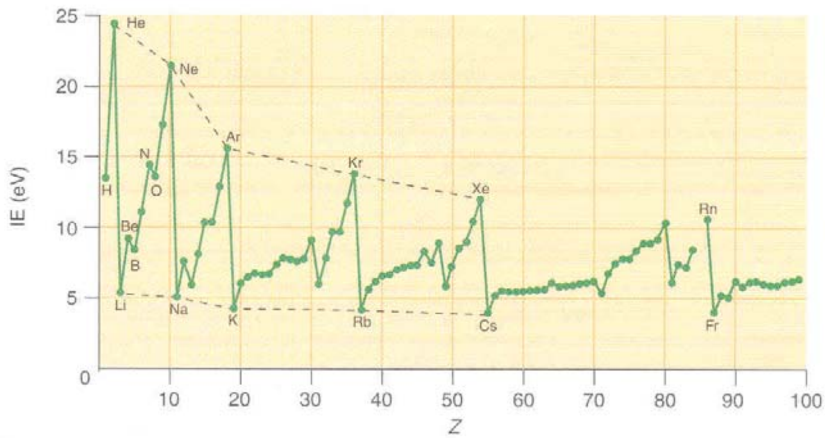


Same periodic trends as atomic radii for a given charge

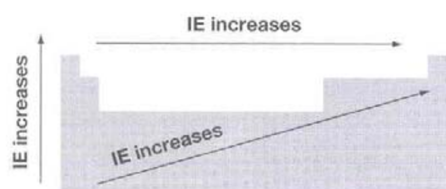


Radius (Å)
Atomic number, Z
0
0.50
1.0
1.5
2.0
10
20
30
40
50
60
Te2−
I−
Se2−
Br−
S2−
Cl−
Xe
Kr
Cs+
Ar
Rb+
O2−
F−
K+
Ba2+
Ne
Sr2+
La3+
Na+
Ca2+
He
Y3+
Ce4+
Sc3+
Zr4+
Mg2+
Ti4+
Li+
Al3+
Si4+
Be2+
B3+
C4+

Figure 4.9: Ionization Energies of the Elements



1 H 13.60																	2 He 24.59
3 Li 5.39	4 Be 9.32											5 B 8.30	6 C 11.26	7 N 14.53	8 O 13.62	9 F 17.42	10 Ne 21.56
11 Na 5.14	12 Mg 7.65											13 Al 5.99	14 Si 8.15	15 P 10.49	16 S 10.36	17 Cl 12.97	18 Ar 15.76
19 K 4.34	20 Ca 6.11	21 Sc 6.56	22 Ti 6.83	23 V 6.75	24 Cr 6.77	25 Mn 7.43	26 Fe 7.90	27 Co 7.88	28 Ni 7.64	29 Cu 7.73	30 Zn 9.39	31 Ga 6.00	32 Ge 7.90	33 As 9.79	34 Se 9.75	35 Br 11.81	36 Kr 14.00
37 Rb 4.18	38 Sr 5.69	39 Y 6.22	40 Zr 6.63	41 Nb 6.76	42 Mo 7.09	43 Tc 7.28	44 Ru 7.36	45 Rh 7.46	46 Pd 8.34	47 Ag 7.58	48 Cd 8.99	49 In 5.79	50 Sn 7.34	51 Sb 8.61	52 Te 9.01	53 I 10.45	54 Xe 12.13
55 Cs 3.89	56 Ba 5.21	57 La 5.58	72 Hf 6.83	73 Ta 7.55	74 W 7.86	75 Re 7.83	76 Os 8.43	77 Ir 8.97	78 Pt 8.96	79 Au 9.23	80 Hg 10.44	81 Tl 6.11	82 Pb 7.42	83 Bi 7.29	84 Po 8.41	85 At	86 Rn 10.75



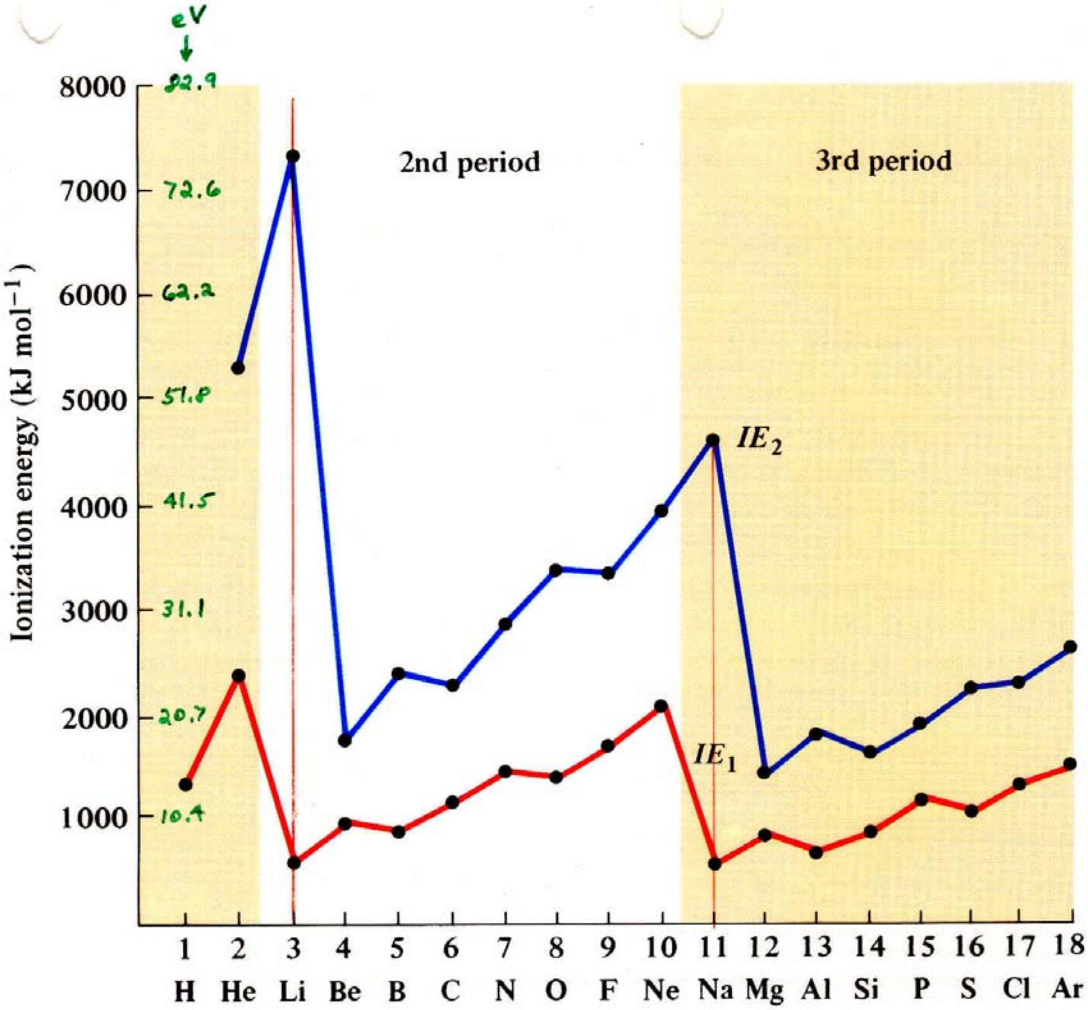
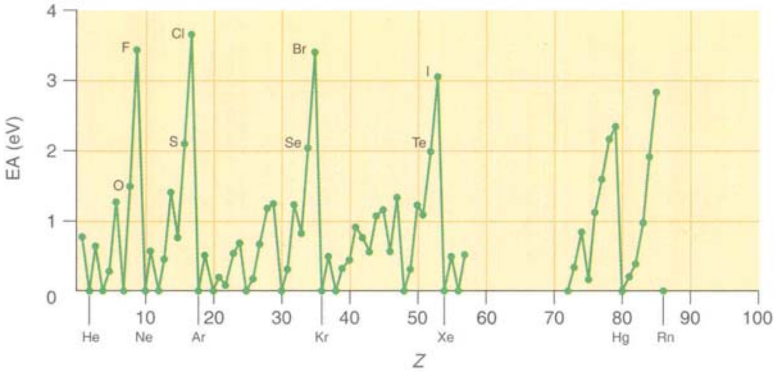

eV
8000
82.9
7000
72.6
6000
62.2
5000
51.8
4000
41.5
3000
31.1
2000
20.7
1000
10.4
Ionization energy (kJ mol^{-1})
2nd period
3rd period
IE_2
IE_1
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar

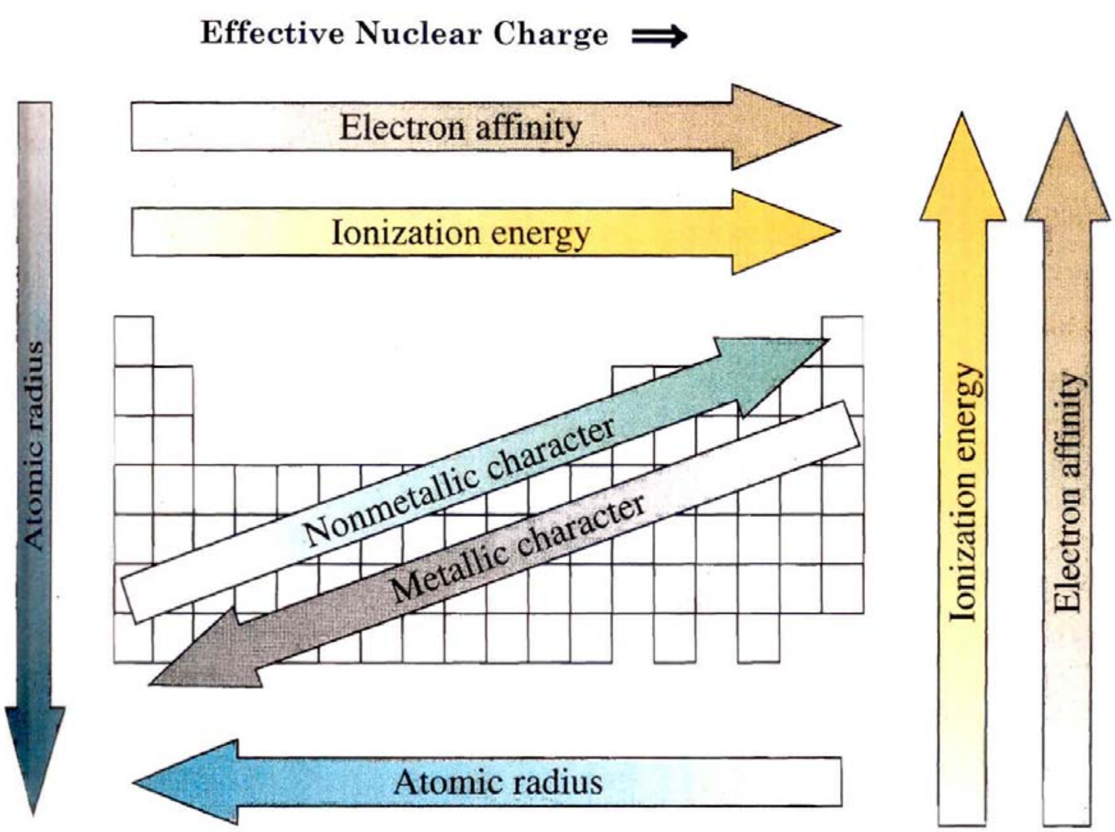
Figure 4.11: Electron Affinities of the Elements



$X^-(g) \longrightarrow X(g) + e^-$ $\Delta E = EA$

1 H 0.754																	2 He 0
3 Li 0.62	4 Be 0											5 B 0.28	6 C 1.263	7 N 0	8 O 1.461	9 F 3.399	10 Ne 0
11 Na 0.55	12 Mg 0											13 Al 0.44	14 Si 1.39	15 P 0.746	16 S 2.077	17 Cl 3.617	18 Ar 0
19 K 0.50	20 Ca 0	21 Sc 0.19	22 Ti 0.08	23 V 0.53	24 Cr 0.67	25 Mn 0	26 Fe 0.16	27 Co 0.66	28 Ni 1.16	29 Cu 1.23	30 Zn 0	31 Ga 0.3	32 Ge 1.2	33 As 0.81	34 Se 2.02	35 Br 3.365	36 Kr 0
37 Rb 0.49	38 Sr 0	39 Y 0.31	40 Zr 0.43	41 Nb 0.89	42 Mo 0.75	43 Tc 0.55	44 Ru 1.05	45 Rh 1.14	46 Pd 0.56	47 Ag 1.30	48 Cd 0	49 In 0.3	50 Sn 1.2	51 Sb 1.07	52 Te 1.97	53 I 3.059	54 Xe 0
55 Cs 0.47	56 Ba 0	57 La 0.5	72 Hf 0	73 Ta 0.32	74 W 0.82	75 Re 0.15	76 Os 1.1	77 Ir 1.57	78 Pt 2.13	79 Au 2.31	80 Hg 0	81 Tl 0.2	82 Pb 0.36	83 Bi 0.95	84 Po 1.9	85 At	86 Rn 0

Summary of Periodic Trends



Summary of Periodic Trends:

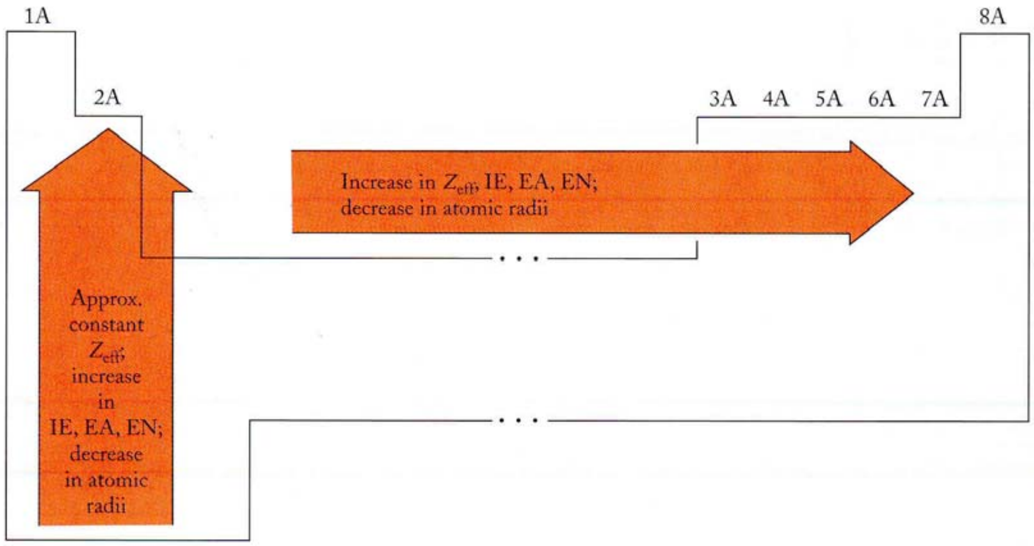


Figure 9.9

A summary of the general vertical and horizontal periodic trends in effective nuclear charge (Z_{eff}), atomic radii (r), ionization energies (IE), electron affinities (EA), and electronegativities (EN). This representation of the periodic law is the first component of the interconnected network of ideas for understanding the periodic table.

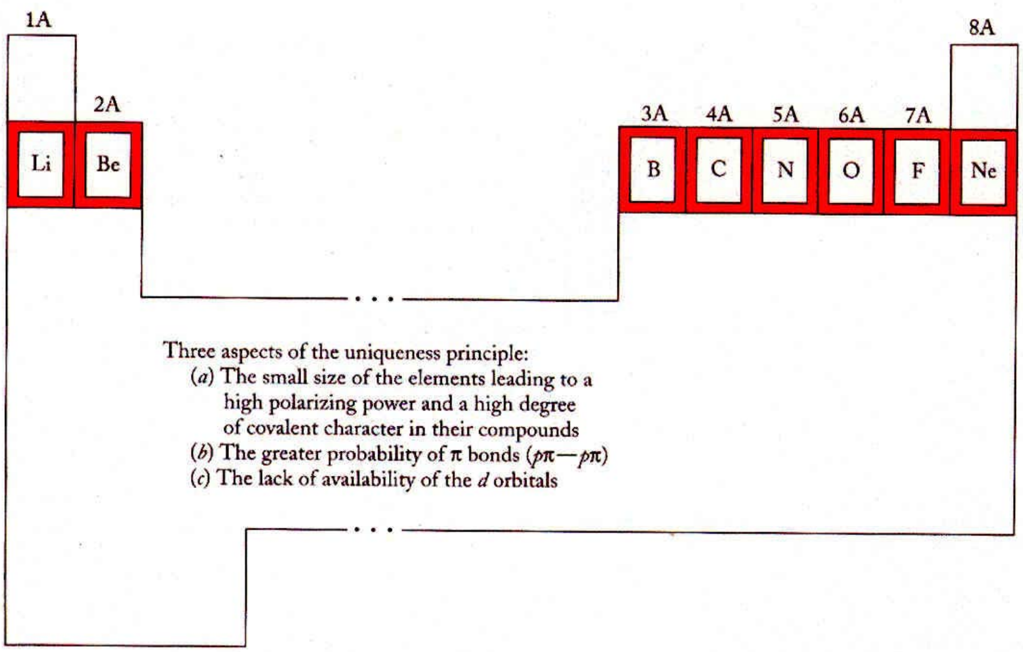


Figure 9.13

A summary of three reasons for the uniqueness principle, which states that the chemistry of the second-period elements (Li, Be, B, C, N, O, F, and Ne) is significantly different from that of their congeners. The uniqueness principle is the second component of the interconnected network of ideas for understanding the periodic table.

FIGURE 9.10

The polarization of the chloride anion by the lithium cation. (*a*) The small Li^+ is able to get very close to the larger, more diffuse electron cloud of Cl^-; (*b*) the electron cloud of Cl^- is distorted, or polarized, by the Li^+; (*c*) the opportunity for overlap between the valence orbitals in Li^+ (empty 2*s*) and the Cl^- (filled 3*p*) is increased.

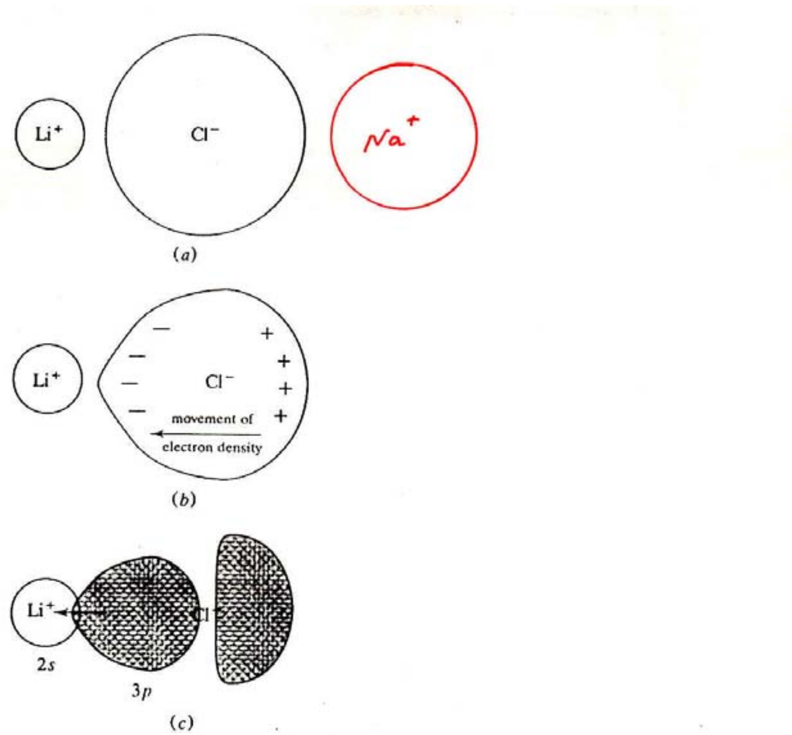


FIGURE 9.11

Parallel orbital overlap, or π bonding, is more effective in (*a*) the smaller first elements—for example, carbon—than it is in (*b*) their larger congeners—for example, silicon.

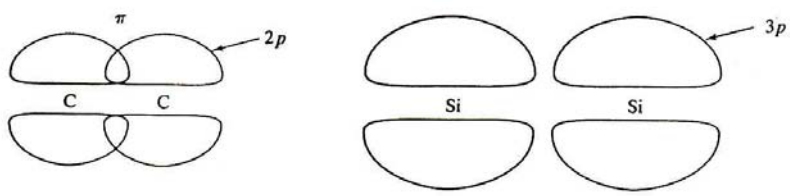


FIGURE 9.12

The availability of *d* orbitals in the heavier congeners of the first elements makes expanded octets possible. (*a*) Carbon is sp^3-hybridized in CF_4. (*b*) Silicon is sp^3d^2-hybridized in SiF_6^{2-}. (*c*) Chlorine is sp^3d-hybridized in ClF_3.

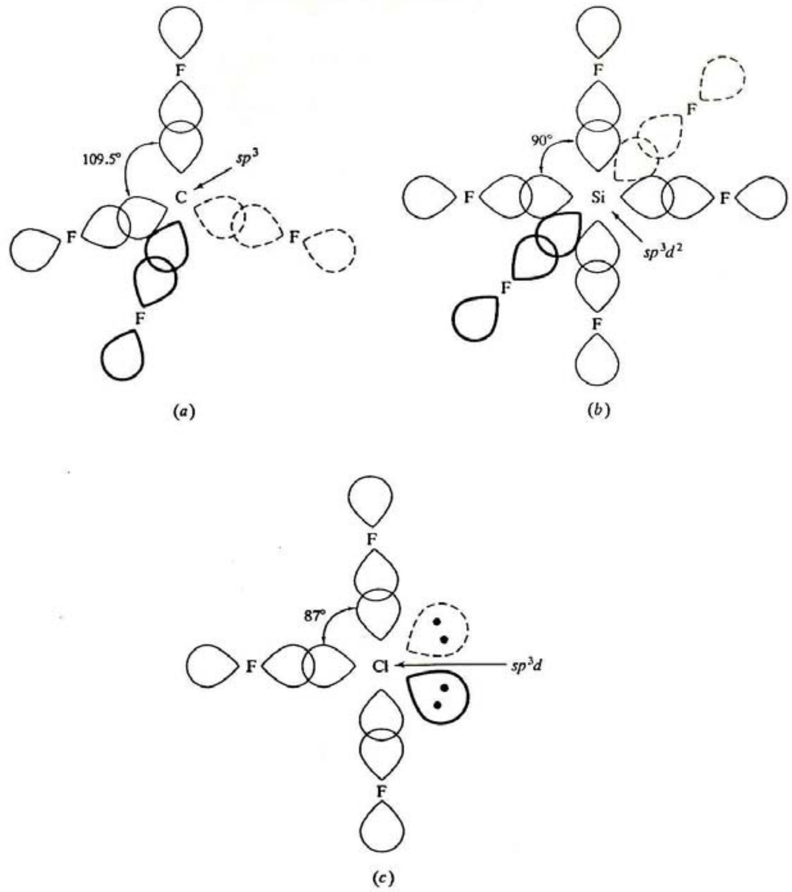


FIGURE 9.14

Four relevant properties of elements related to the diagonal effect.

	Li	Be	B	C
Charge of ion	+1	+2	+3	+4
Ionic radius, Å[a]	0.73	0.41	0.25	0.29
Charge density	1.4	4.9	12	14
Electronegativity	1.0	1.5	2.0	2.5
	Na	Mg	Al	Si
Charge of ion	+1	+2	+3	+4
Ionic radius, Å	1.13	0.71	0.53	0.40
Charge density	0.88	2.8	5.7	10
Electronegativity	0.9	1.2	1.5	1.8

[a] Shannon-Prewitt radii for C.N. = 4. (See discussion in Section 7.3 for further information.)

The Diagonal Effect

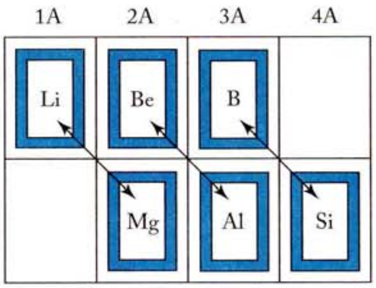
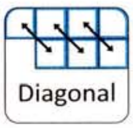
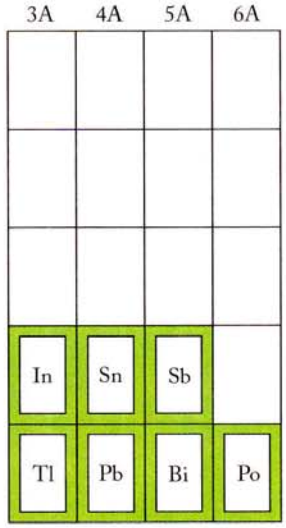


FIGURE 9.16

The elements of the diagonal effect. Lithium and magnesium, beryllium and aluminum, and boron and silicon, each pair diagonally located, have similar properties. The diagonal effect is the third component of the network of interconnected ideas for understanding the periodic table.



The Inert-Pair Effect



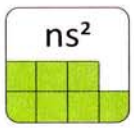


FIGURE 9.18

The inert-pair effect. The elements of the inert-pair effect. The elements shown form compounds where the oxidation state is 2 less than the expected group valence. The inert-pair effect is the fourth component of the interconnected network of ideas for understanding the periodic table.

The Metal-Nonmetal Line

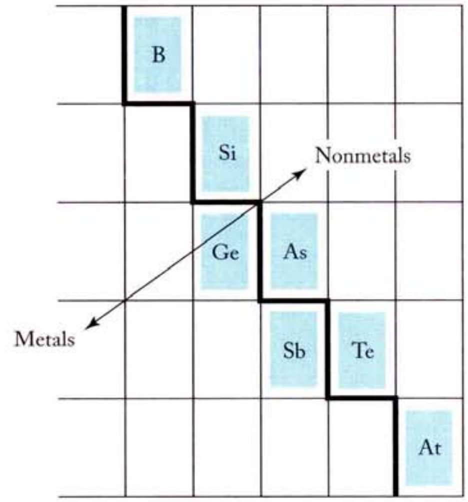
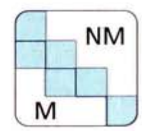


FIGURE 9.19

The metal–nonmetal line in the periodic table. Elements to the lower left are metals; elements to the upper right are nonmetals. The metalloids, or semimetals, are shaded. The metal-nonmetal line is the fifth component of the interconnected network of ideas for understanding the periodic table.



The Network of Interconnected Ideas: The First Five Components

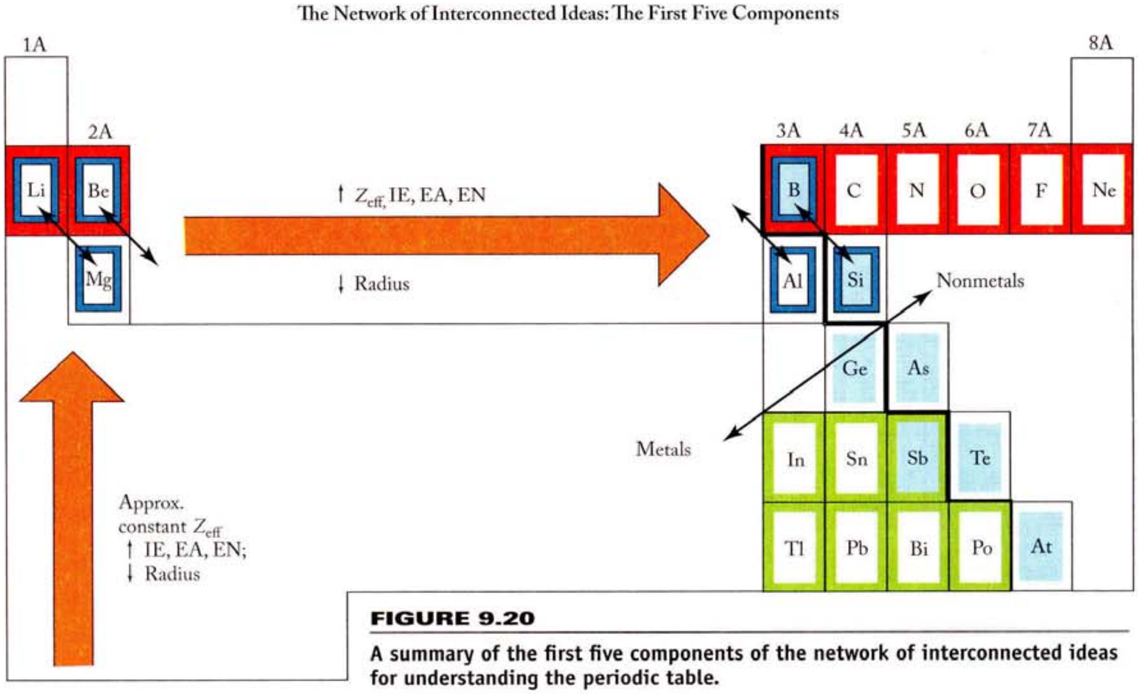
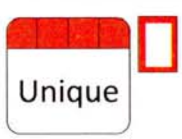


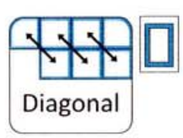
FIGURE 9.20

A summary of the first five components of the network of interconnected ideas for understanding the periodic table.

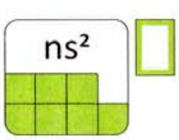
The Periodic Law (See p. 225)



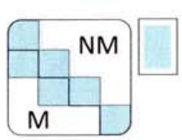
The Uniqueness Principle (See p. 241)



The Diagonal Effect (See p. 242)



The Inert-Pair Effect (See p. 244)



The Metal-Nonmetal Line (See p. 246)