# First ionization Energy plot (Energy versus atomic number)

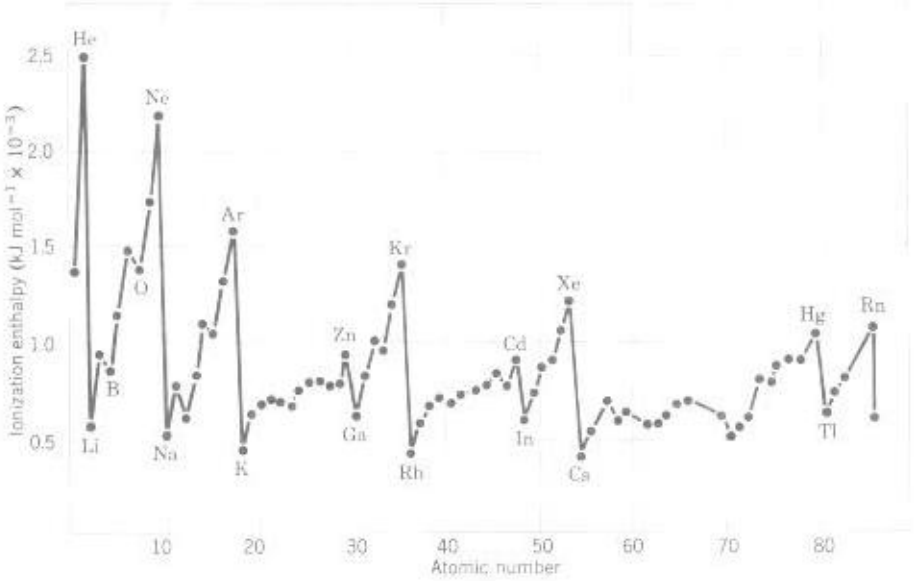



**Figure 2-14** Periodic trends in the first ionization enthalpies, $\Delta H_{ion_1}$. Values for the first ionization enthalpies of the elements are also listed in Appendix IIIB.

**Table 1.6** Ionization energies of the elements* (in eV; 1 eV/atom = 96.4869 kJ/mole) *(Continued)*

| Z | Element | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|---|
| 40 | Zr | 6.84 | 13.13 | 22.99 | 34.34 | 81.5 | | | |
| 41 | Nb | 6.88 | 14.32 | 25.04 | 38.3 | 50.55 | 102.6 | 125 | |
| 42 | Mo | 7.099 | 16.15 | 27.16 | 46.4 | 61.2 | 68 | 126.8 | 153 |
| 43 | Tc | 7.28 | 15.26 | 29.54 | | | | | |
| 44 | Ru | 7.37 | 16.76 | 28.47 | | | | | |
| 45 | Rh | 7.46 | 18.08 | 31.06 | | | | | |
| 46 | Pd | 8.34 | 19.43 | 32.93 | | | | | |
| 47 | Ag | 7.576 | 21.49 | 34.83 | | | | | |
| 48 | Cd | 8.993 | 16.908 | 37.48 | | | | | |
| 49 | In | 5.786 | 18.869 | 28.03 | 54 | | | | |
| 50 | Sn | 7.344 | 14.632 | 30.502 | 40.734 | 72.28 | | | |
| 51 | Sb | 8.641 | 16.53 | 25.3 | 44.2 | 56 | 108 | | |
| 52 | Te | 9.009 | 18.6 | 27.96 | 37.41 | 58.75 | 70.7 | 137 | |
| 53 | I | 10.451 | 19.131 | 33 | | | | | |
| 54 | Xe | 12.130 | 21.21 | 32.1 | | | | | |
| 55 | Cs | 3.894 | 25.1 | | | | | | |
| 56 | Ba | 5.212 | 10.004 | | | | | | |
| 57 | La | 5.577 | 11.06 | 19.175 | | | | | |
| 58 | Ce | 5.47 | 10.85 | 20.20 | 36.72 | | | | |
| 59 | Pr | 5.42 | 10.55 | 21.62 | 38.95 | 57.45 | | | |
| 60 | Nd | 5.49 | 10.72 | | | | | | |
| 61 | Pm | 5.55 | 10.90 | | | | | | |
| 62 | Sm | 5.63 | 11.07 | | | | | | |
| 63 | Eu | 5.67 | 11.25 | | | | | | |
| 64 | Gd | 6.14 | 12.1 | | | | | | |
| 65 | Tb | 5.85 | 11.52 | | | | | | |
| 66 | Dy | 5.93 | 11.67 | | | | | | |
| 67 | Ho | 6.02 | 11.80 | | | | | | |
| 68 | Er | 6.10 | 11.93 | | | | | | |
| 69 | Tm | 6.18 | 12.05 | 23.71 | | | | | |
| 70 | Yb | 6.254 | 12.17 | 25.2 | | | | | |
| 71 | Lu | 5.426 | 13.9 | | | | | | |
| 72 | Hf | 7.0 | 14.9 | 23.3 | 33.3 | | | | |
| 73 | Ta | 7.89 | | | | | | | |
| 74 | W | 7.98 | | | | | | | |
| 75 | Re | 7.88 | | | | | | | |
| 76 | Os | 8.7 | | | | | | | |
| 77 | Ir | 9.1 | | | | | | | |
| 78 | Pt | 9.0 | 18.563 | | | | | | |
| 79 | Au | 9.225 | 20.5 | | | | | | |
| 80 | Hg | 10.437 | 18.756 | 34.2 | | | | | |
| 81 | Tl | 6.108 | 20.428 | 29.83 | | | | | |
| 82 | Pb | 7.416 | 15.032 | 31.937 | 42.32 | 68.8 | | | |
| 83 | Bi | 7.289 | 16.69 | 25.56 | 45.3 | 56.0 | 88.3 | | |
| 84 | Po | 8.42 | | | | | | | |
| 85 | At | | | | | | | | |
| 86 | Rn | 10.748 | | | | | | | |
| 87 | Fr | | | | | | | | |
| 88 | Ra | 5.279 | 10.147 | | | | | | |
| 89 | Ac | 6.9 | 12.1 | | | | | | |
| 90 | Th | | 11.5 | 20.0 | 28.8 | | | | |
| 91 | Pa | | | | | | | | |
| 92 | U | | | | | | | | |
| 93 | Np | | | | | | | | |
| 94 | Pu | 5.8 | | | | | | | |
| 95 | Am | 6.0 | | | | | | | |

*From C. E. Moore, "Ionization Potentials and Ionization Limits from Atomic Spectra," NSRDS-NBS 34, 1970.

Ionization Energies

1st I.E.

2nd I.E.

3rd I.E. etc.



Table 1.6 Ionization energies of the elements[a] (in eV; 1 eV/atom = 96.4869 kJ/mole)

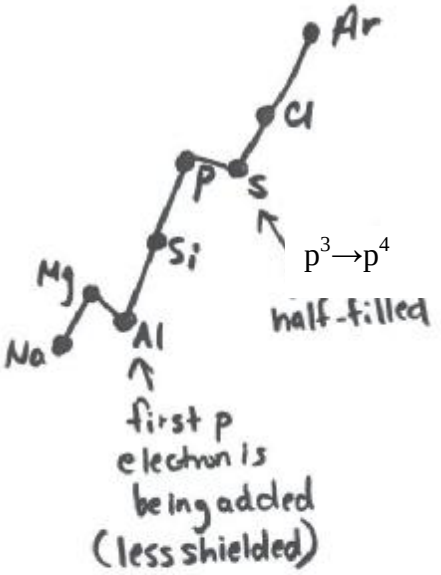
| Z | Element | I | II | III | IV | V | VI | VII | VIII |
|---|---|---|---|---|---|---|---|---|---|
| 1 | H | 13.598 | | | | | | | |
| 2 | He | 24.587 | 54.416 | | | | | | |
| 3 | Li | 5.392 | 75.638 | 122.451 | | | | | |
| 4 | Be | 9.322 | 18.211 | 153.893 | 217.713 | | | | |
| 5 | B | 8.298 | 25.154 | 37.930 | 259.368 | 340.217 | | | |
| 6 | C | 11.260 | 24.383 | 47.887 | 64.492 | 392.077 | 489.981 | | |
| 7 | N | 14.534 | 29.601 | 47.448 | 77.472 | 97.888 | 552.057 | 667.029 | |
| 8 | O | 13.618 | 35.116 | 54.934 | 77.412 | 113.896 | 138.116 | 739.315 | 871.387 |
| 9 | F | 17.422 | 34.970 | 62.707 | 87.138 | 114.240 | 157.161 | 185.182 | 953.886 |
| 10 | Ne | 21.564 | 40.962 | 63.45 | 97.11 | 126.21 | 157.93 | 207.27 | 239.09 |
| 11 | Na | 5.139 | 47.286 | 71.64 | 98.91 | 138.39 | 172.15 | 208.47 | 264.18 |
| 12 | Mg | 7.646 | 15.035 | 80.143 | 109.24 | 141.26 | 186.50 | 224.94 | 265.90 |
| 13 | Al | 5.986 | 18.828 | 28.447 | 119.99 | 153.71 | 190.47 | 241.43 | 284.59 |
| 14 | Si | 8.151 | 16.345 | 33.492 | 45.141 | 166.77 | 205.05 | 246.52 | 303.17 |
| 15 | P | 10.486 | 19.725 | 30.18 | 51.37 | 65.023 | 220.43 | 263.22 | 309.41 |
| 16 | S | 10.360 | 23.33 | 34.83 | 47.30 | 72.68 | 88.049 | 280.93 | 328.23 |
| 17 | Cl | 12.967 | 23.81 | 39.61 | 53.46 | 67.8 | 97.03 | 114.193 | 348.28 |
| 18 | Ar | 15.759 | 27.629 | 40.74 | 59.81 | 75.02 | 91.007 | 124.319 | 143.456 |
| 19 | K | 4.341 | 31.625 | 45.72 | 60.91 | 82.66 | 100.0 | 117.56 | 154.86 |
| 20 | Ca | 6.113 | 11.871 | 50.908 | 67.10 | 84.41 | 108.78 | 127.7 | 147.24 |
| 21 | Sc | 6.54 | 12.80 | 24.76 | 73.47 | 91.66 | 111.1 | 138.0 | 158.7 |
| 22 | Ti | 6.82 | 13.58 | 27.491 | 43.266 | 99.22 | 119.36 | 140.8 | 168.5 |
| 23 | V | 6.74 | 14.65 | 29.310 | 46.707 | 65.23 | 128.12 | 150.17 | 173.7 |
| 24 | Cr | 6.766 | 16.50 | 30.96 | 49.1 | 69.3 | 90.56 | 161.1 | 184.7 |
| 25 | Mn | 7.435 | 15.640 | 33.667 | 51.2 | 72.4 | 95 | 119.27 | 196.46 |
| 26 | Fe | 7.870 | 16.18 | 30.651 | 54.8 | 75.0 | 99 | 125 | 151.06 |
| 27 | Co | 7.86 | 17.06 | 33.50 | 51.3 | 79.5 | 102 | 129 | 157 |
| 28 | Ni | 7.635 | 18.168 | 35.17 | 54.9 | 75.5 | 108 | 133 | 162 |
| 29 | Cu | 7.726 | 20.292 | 36.83 | 55.2 | 79.9 | 103 | 139 | 166 |
| 30 | Zn | 9.394 | 17.964 | 39.722 | 59.4 | 82.6 | 108 | 134 | 174 |
| 31 | Ga | 5.999 | 20.51 | 30.71 | 64 | | | | |
| 32 | Ge | 7.899 | 15.934 | 34.22 | 45.71 | 93.5 | | | |
| 33 | As | 9.81 | 18.633 | 28.351 | 50.13 | 62.63 | 127.6 | | |
| 34 | Se | 9.752 | 21.19 | 30.820 | 42.944 | 68.3 | 81.70 | 155.4 | |
| 35 | Br | 11.814 | 21.8 | 36 | 47.3 | 59.7 | 88.6 | 103.0 | 192.8 |
| 36 | Kr | 13.999 | 24.359 | 36.95 | 52.5 | 64.7 | 78.5 | 111.0 | 126 |
| 37 | Rb | 4.177 | 27.28 | 40 | 52.6 | 71.0 | 84.4 | 99.2 | 136 |
| 38 | Sr | 5.695 | 11.030 | 43.6 | 57 | 71.6 | 90.8 | 106 | 122.3 |
| 39 | Y | 6.38 | 12.24 | 20.52 | 61.8 | 77.0 | 93.0 | 116 | 129 |

(Continued)

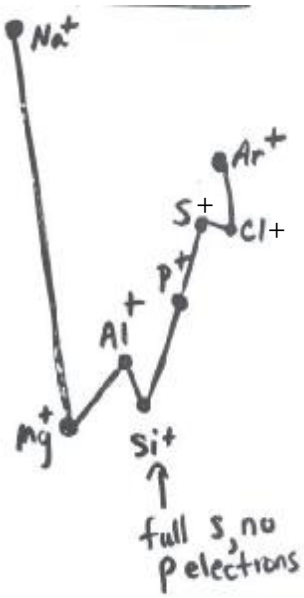
100K at

# Ionization Energies

1st I.E.




2nd I.E.




Overall trend of increasing I.E. from left to right is evident, but major exceptions in the second I.E.

# Atomic Radii

1. Single – bond covalent radius ($r_{cov}$)
   of an element. Used in bond length determination.

2. van der waals radius ($r_{vdw}$)
   non-bonded distance of two atoms that are touching one another.

3. ionic radius ($r_{ion}$)
   Radius used in ionic compounds
   these have been tabulated and are additive.

Page 61, Table 2-15

$Na^+$ 1.16 Å (116 pm)  $Cl^-$ 1.67 Å (167 pm)

Therefore NaCl internuclear separation is 2.83 Å

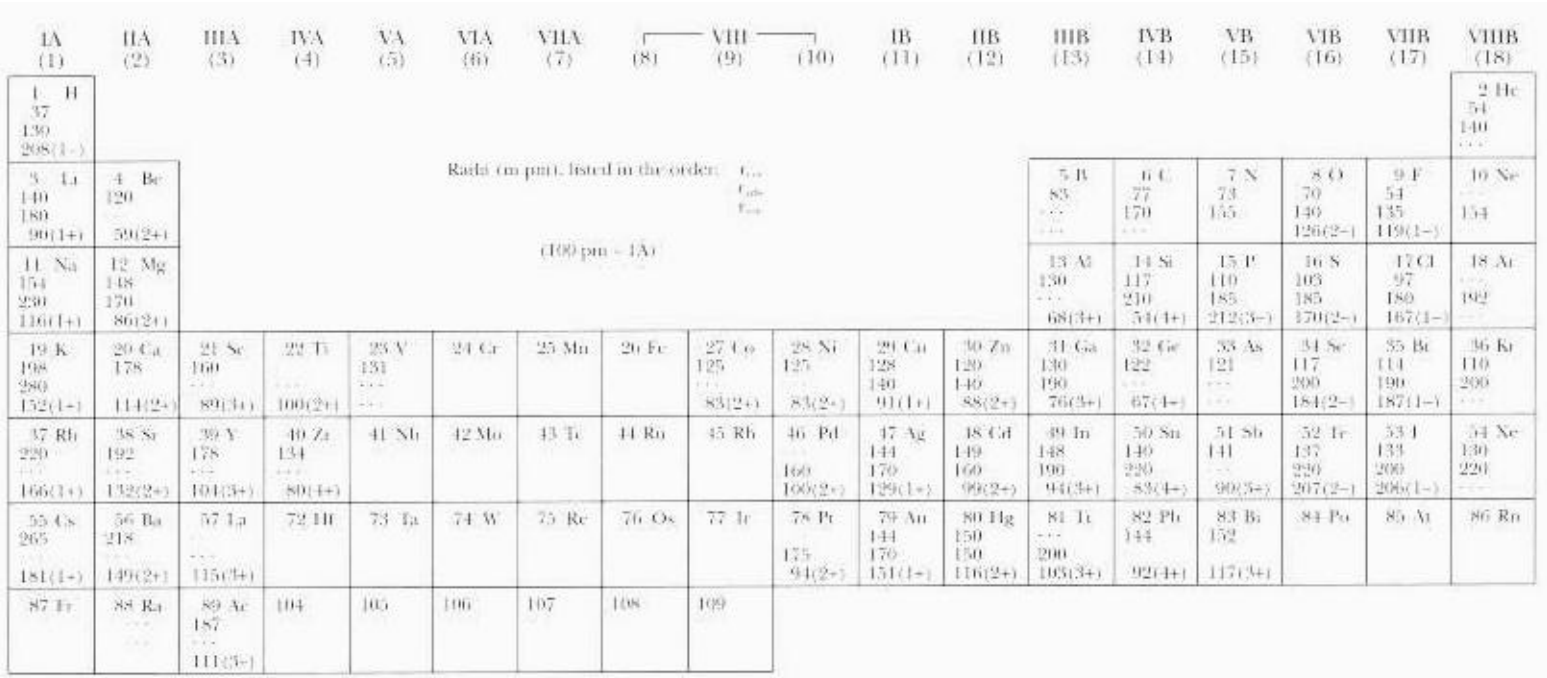



**Figure 2-15** Periodic trends in atomic and ionic radii. For each element, the top value is the average single-bond covalent radius $r_{cov}$; the middle value is the average van der Waals radius $r_{vdw}$; the bottom value is the "Shannon and Prewitt" ionic radius $r_{ion}$ for the oxidation state that is specified in parentheses, as described in the text. Each radius is given in picometers (pm), one angstrom (Å) being equal to 100 pm.

# Atomic Radii & van der Waals radii

1. Alkali metals are largest

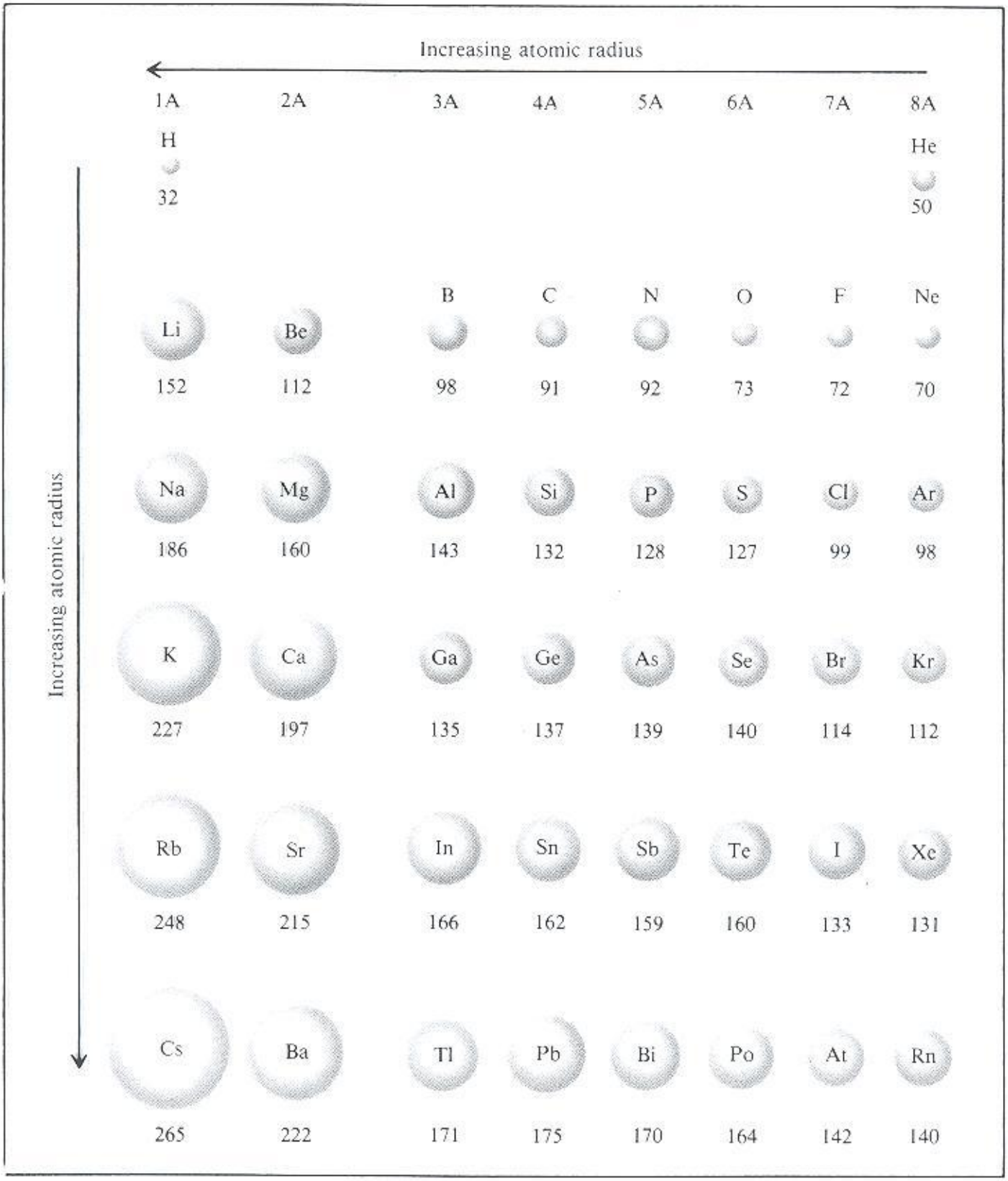
2. Halogens (noble gases) are smallest  Why?

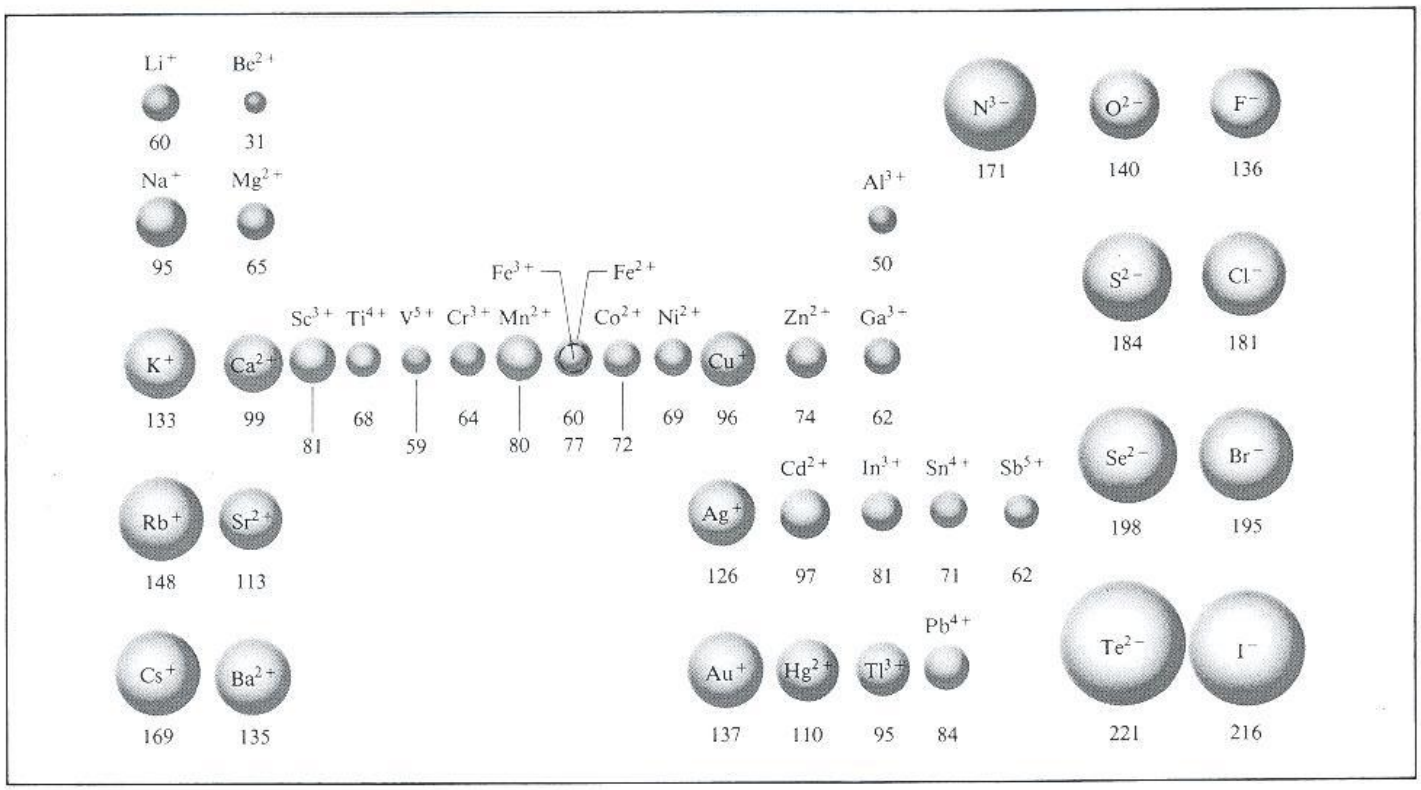
   (page 62. Effective nuclear charge increases but electrons in the orbitals added to the same level, n, are progressively less shielded from the increasing positive charge of the nucleus from each added proton)

## Ionic Radii

1. Alkali metals become positively charged (lose $e^-$'s) so they are smallest.

2. Halogens become negatively charged (gain $e^-$'s) so they are largest.


Increasing atomic radius
Increasing atomic radius
1A
2A
3A
4A
5A
6A
7A
8A
H
32
He
50
B
C
N
O
F
Ne
Li
Be
152
112
98
91
92
73
72
70
Na
Mg
Al
Si
P
S
Cl
Ar
186
160
143
132
128
127
99
98
K
Ca
Ga
Ge
As
Se
Br
Kr
227
197
135
137
139
140
114
112
Rb
Sr
In
Sn
Sb
Te
I
Xe
248
215
166
162
159
160
133
131
Cs
Ba
Tl
Pb
Bi
Po
At
Rn
265
222
171
175
170
164
142
140




# Electron Affinities
## (Electron Attachment Enthalpies)

$\Delta H_{ea}$

Tendency of an atom to form an anion

$-\Delta H_{ea}$

Means exothermic so the more negative the number, the more favorable

1. Alkali metals have mostly positive (endothermic) $\Delta H_{ea}$, but most positive are Be, Mg, Ca (alkaline earths)

   Going from $ns^2$ to $ns^2np^1$ or $ns^2(n-1)d^1$ is not favorable

   Closed shell is favorable.

2. The most negative $\Delta H_{ea}$ values are for the halogens which have a great tendency to achieve the noble gas configuration

   $np^5 \xrightarrow{+e^-} np^6$
   $F \rightarrow F^-$
   $Cl \rightarrow Cl^-$

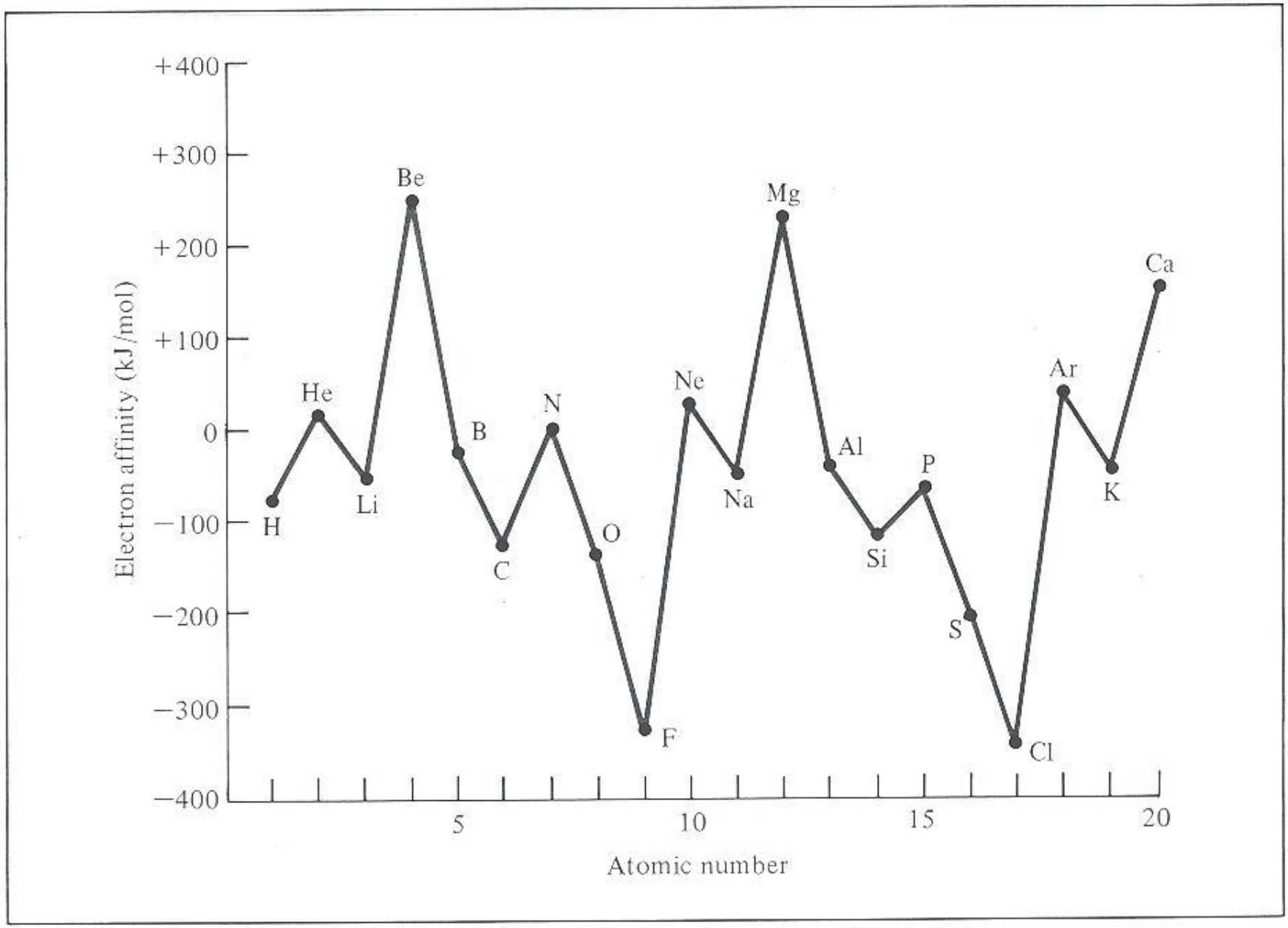
## Electronegativites

Empirical measure of the tendency of an atom in a molecule to attract the electrons in a bond.

Called $\chi$ (chi).

Is not the same as $\Delta H_{ea}$, although they are related

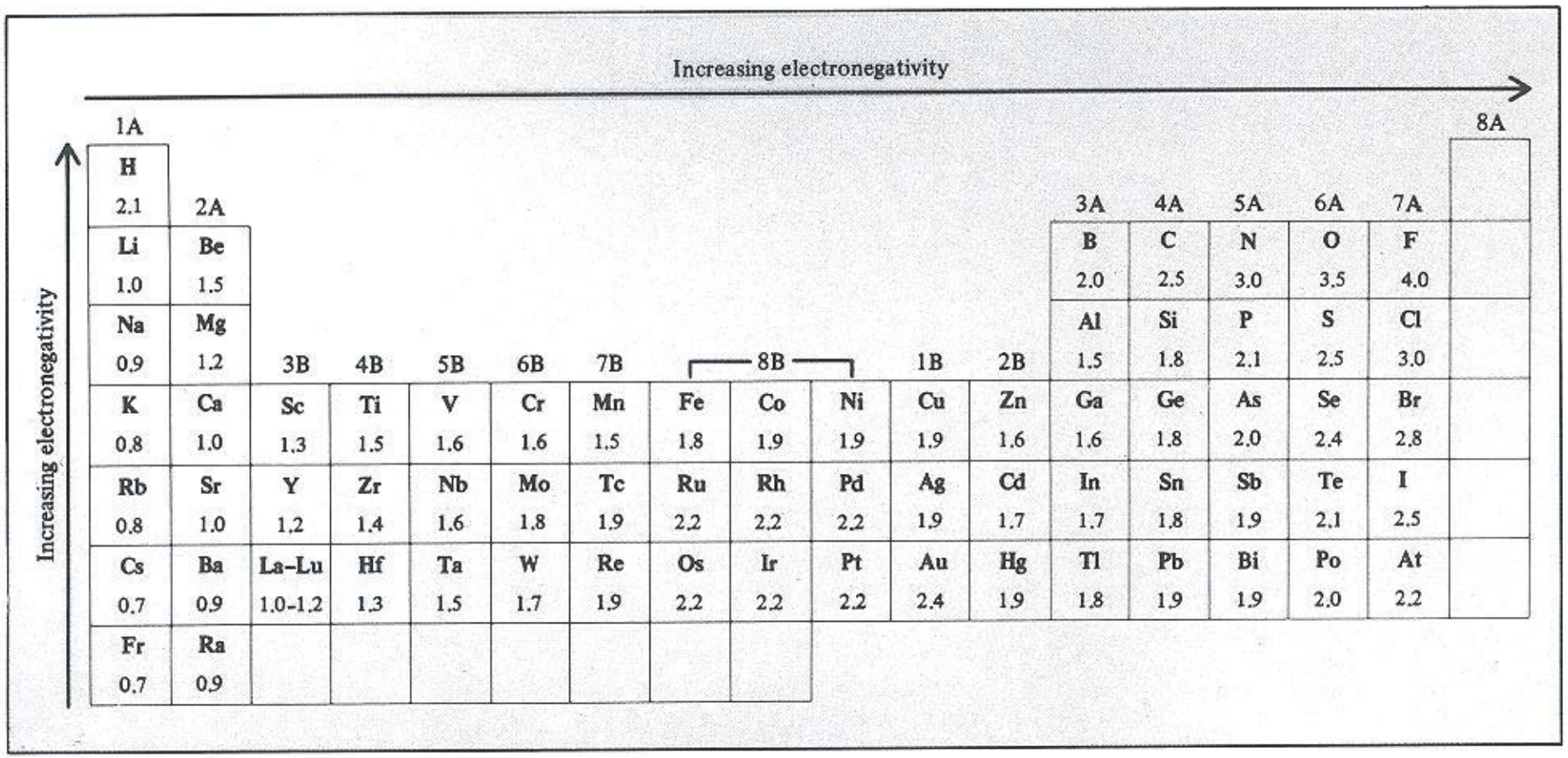
Figure 8.15



There are essentially three ways to determine "or calculate" Electronegativities

1) Pauling 2) Allred & Rochow 3) Mulliken ← first

Figure 9.8




| 1A | | | | | | | | | | | | 3A | 4A | 5A | 6A | 7A | 8A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| H 2.1 | 2A | | | | | | | | | | | | | | | | |
| Li 1.0 | Be 1.5 | | | | | | | | | | | B 2.0 | C 2.5 | N 3.0 | O 3.5 | F 4.0 | |
| Na 0.9 | Mg 1.2 | 3B | 4B | 5B | 6B | 7B | | 8B | | 1B | 2B | Al 1.5 | Si 1.8 | P 2.1 | S 2.5 | Cl 3.0 | |
| K 0.8 | Ca 1.0 | Sc 1.3 | Ti 1.5 | V 1.6 | Cr 1.6 | Mn 1.5 | Fe 1.8 | Co 1.9 | Ni 1.9 | Cu 1.9 | Zn 1.6 | Ga 1.6 | Ge 1.8 | As 2.0 | Se 2.4 | Br 2.8 | |
| Rb 0.8 | Sr 1.0 | Y 1.2 | Zr 1.4 | Nb 1.6 | Mo 1.8 | Tc 1.9 | Ru 2.2 | Rh 2.2 | Pd 2.2 | Ag 1.9 | Cd 1.7 | In 1.7 | Sn 1.8 | Sb 1.9 | Te 2.1 | I 2.5 | |
| Cs 0.7 | Ba 0.9 | La–Lu 1.0–1.2 | Hf 1.3 | Ta 1.5 | W 1.7 | Re 1.9 | Os 2.2 | Ir 2.2 | Pt 2.2 | Au 2.4 | Hg 1.9 | Tl 1.8 | Pb 1.9 | Bi 1.9 | Po 2.0 | At 2.2 | |
| Fr 0.7 | Ra 0.9 | | | | | | | | | | | | | | | | |

# Chapter 3 Structure and Bonding in Molecules

- Our current understanding of bonding is quite high due to the use of X-ray crystallography and spectroscopy. We can make detailed predictions and comparisons based on a large database of experimental evidence.

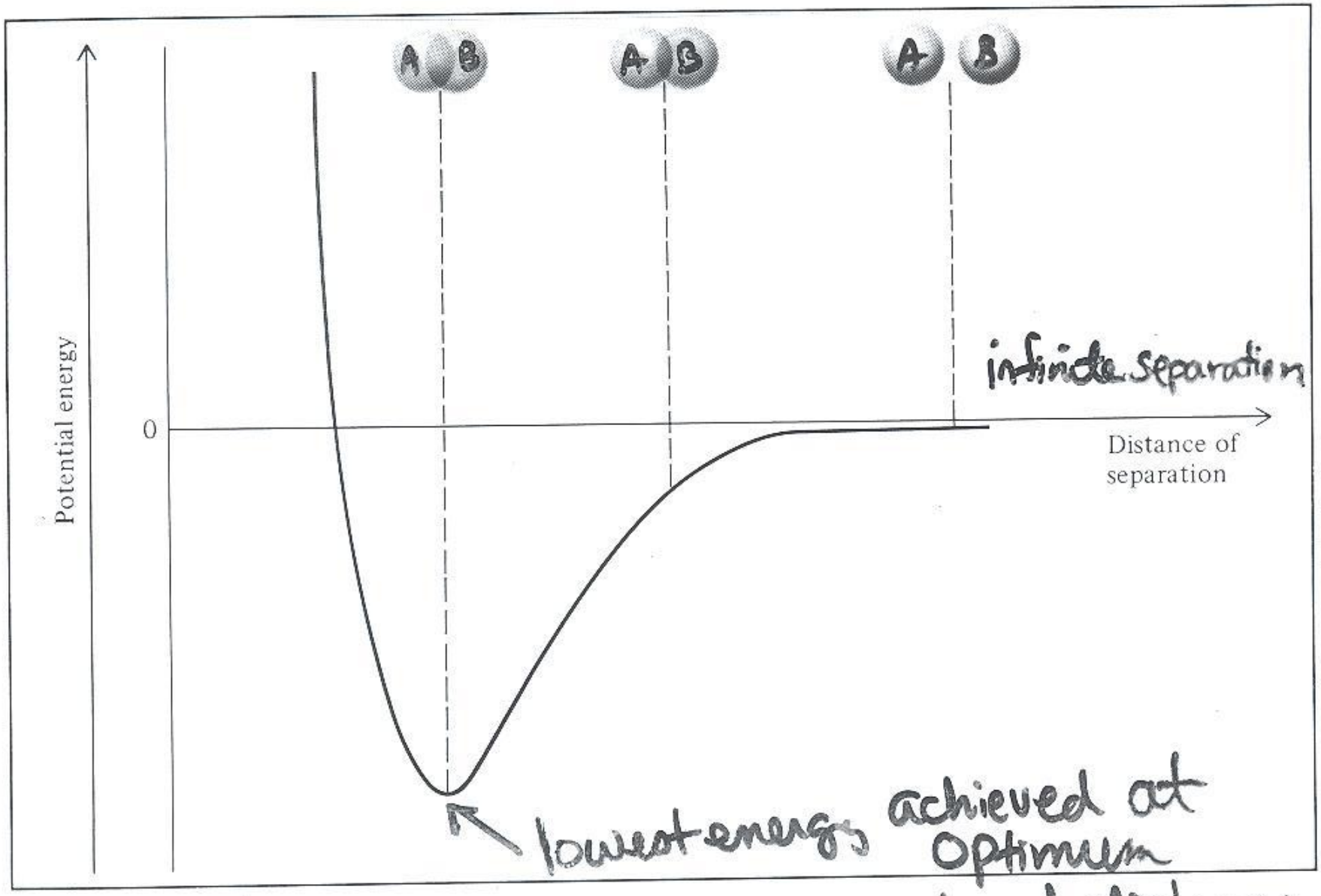
- In the absence of detailed data

  → Models

  Many different levels of Bonding Theories exist

# P.E. versus Distance Between Atoms A & B

Figure 10.6



## Two Main Types:

- Localized bonding Theories
- Delocalized Bonding Theories

Chapter 2 – Electronic Structure – and orbitals are very important to bear in mind for the models.

Electrons → orbitals → bonds

## Three types of Bonding:

1. Covalent (two-center) bonding between pairs of electrons (localized)

2. Delocalized covalent bonding (multicenter bonding)

3. Ionic Bonding

In this section, localized and delocalized covalent bonding will be discussed. Ionic Bonding is really a separate subject, as it treats the bond as a purely electrostatic attraction.

Important Point while you are studying the subject of covalent bonding:

There are three theories that are presented together as inter-related topics

1. Lewis Dot structures (electron –pairs)

2. VSEPR Theory: valence shell electron pair repulsion theory

3. Hybridization

## 1. Lewis Concept  Localized Electron Pairs

G. N. Lewis - Bonding involves a sharing of electrons

Bonding Pairs

A : B

Pairs of electrons between two atoms lead to a covalent bond

→ localized between two atoms

Lone Pairs

: A : B

A lone pair is localized on one atom here

Electronic Structure based on this model is the sum of all the bonding pairs and lone pairs.

We use a diagram to represent this → Lewis Diagram

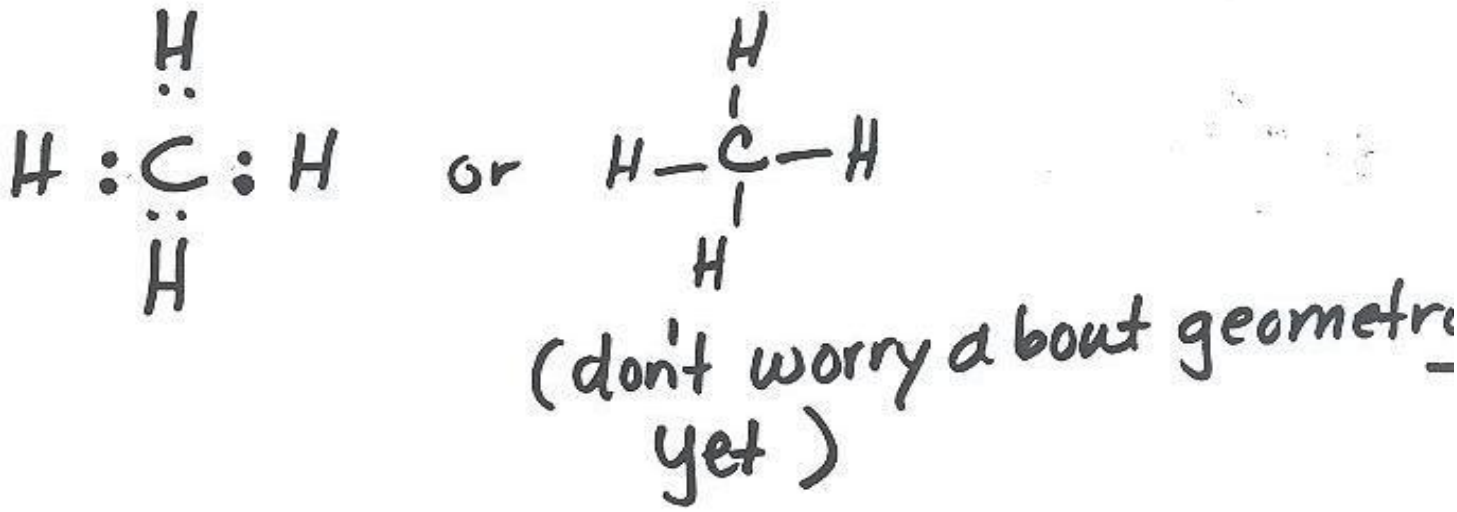
# Lewis Diagrams

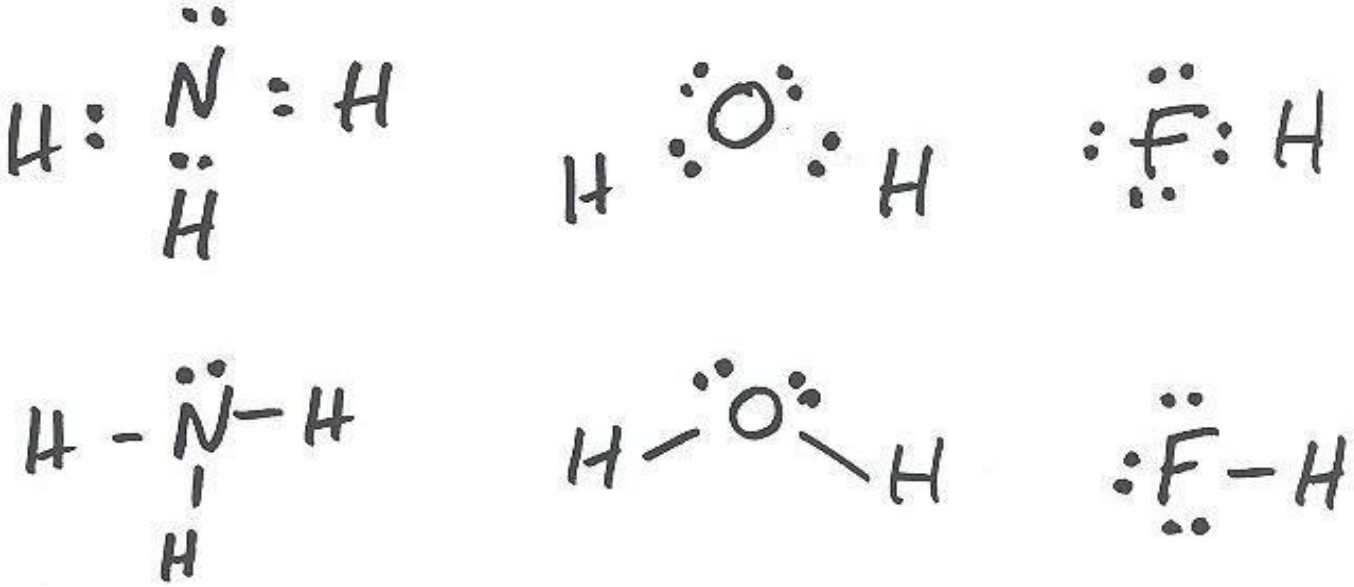
- Use only valence electrons
- Electrons are either involved in a two electron bond or they are localized as a lone pair (or lone electrons)
- Bear in mind that the simplest, most symmetrical structure is typically correct
- The central atom is typically:
  - A metal (or at least electron e.g. atom)
  - Odd atom in the formula
  - Never hydrogen
- Atoms usually need to achieve a full octet (exceptions are B, Be, Al) if they are in the $1^{st}$ and $2^{nd}$ periods
- Atoms beyond $2^{nd}$ row, atom can acquire more than an octet.

→ valence shell expansion

A. Octet Systems

1. Saturated Systems – Single bonds only



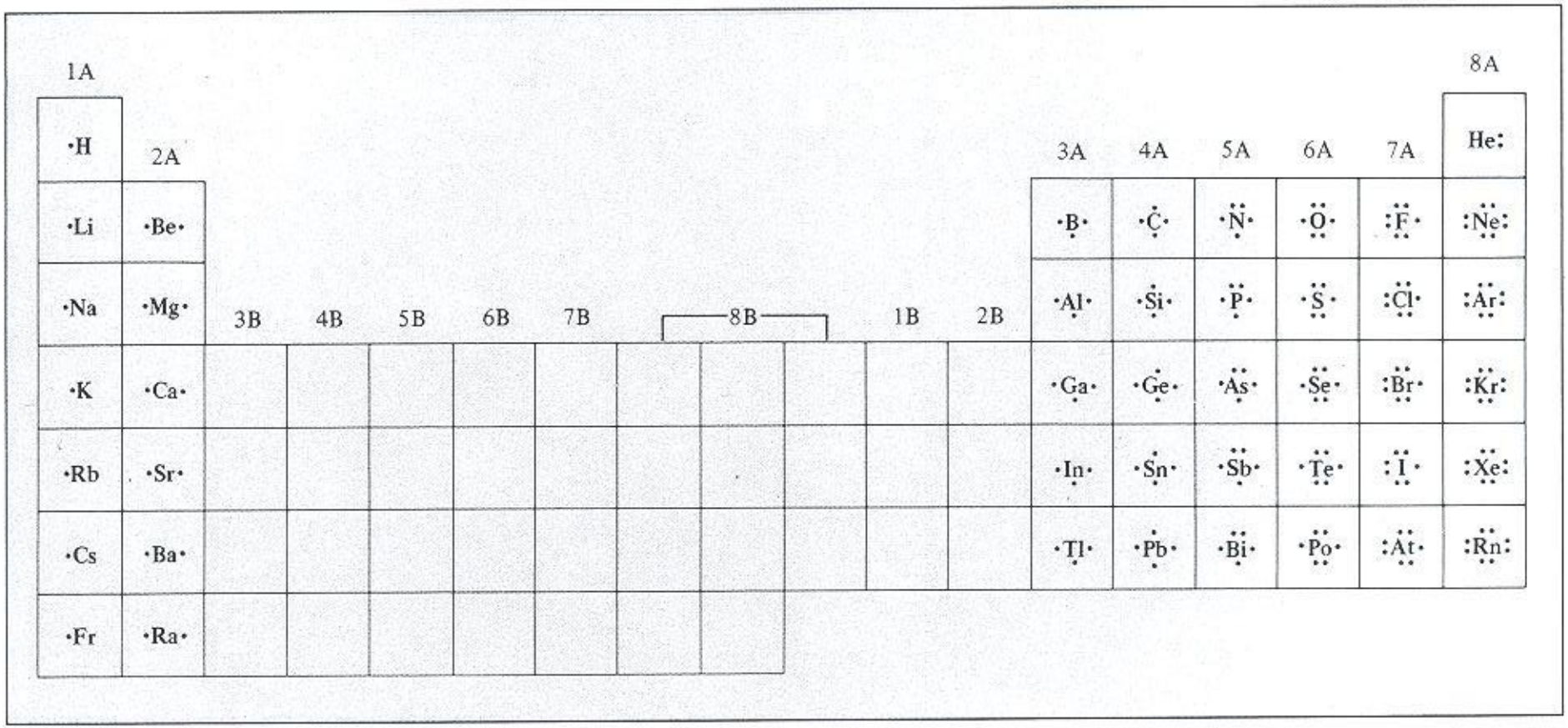
---

| | | | | |
|---|---|---|---|---|
| C | $4e^-$ | O | $6e^-$ | Valence |
| N | $5e^-$ | F | $7e^-$ | electron |
| H | $1e^-$ | | | counts |

Same as group in Periodic Table

Figure 9.1

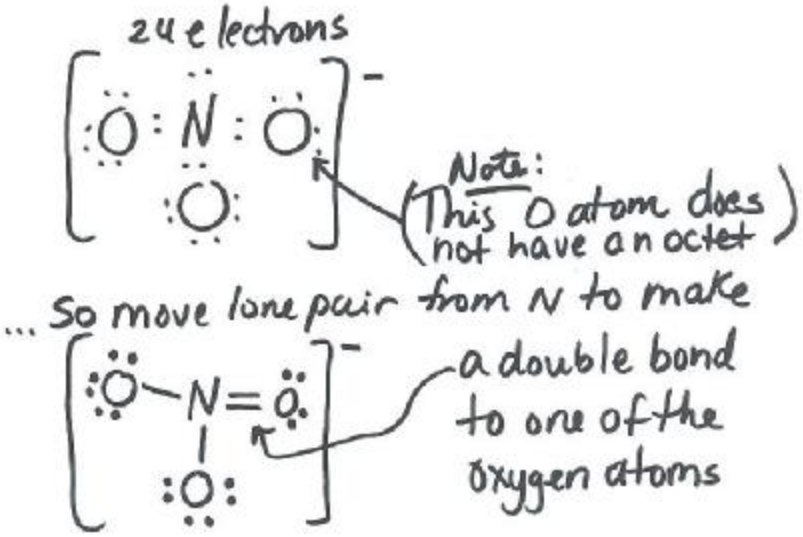
Lewis Dot symbols for the various elements



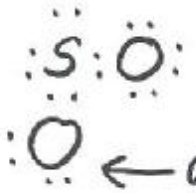
2. Unsaturated – multiple bonds are required for atoms to achieve a full octet.

e.g., $NO_3^-$, $SO_2$

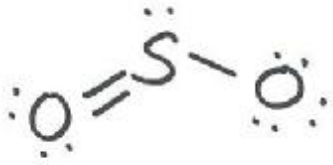
| | | | |
|---|---|---|---|
| $NO_3^-$ | N | 5 electrons | 5 |
| | O | 6 electrons x 3 | 18 |
| | 1 | extra electron | 1 |
| | | | 24 electrons |




| | | | |
|---|---|---|---|
| $SO_2$ | S | 6 electrons | 6 |
| | O | 6 electrons x 2 | 12 |
| | | | 18 electrons |



← again, this O atom is deficient



Better structure is this one

Q. What about $CO_2$?

| | | |
|---|---|---|
| C | 4 electrons | 4 |
| O | 6 electrons x 2 | 12 |
| | | 16 $e^-$ |

A.