Lecture 7 January 2019

Electronegativity Scales

Electric Dipole Moments

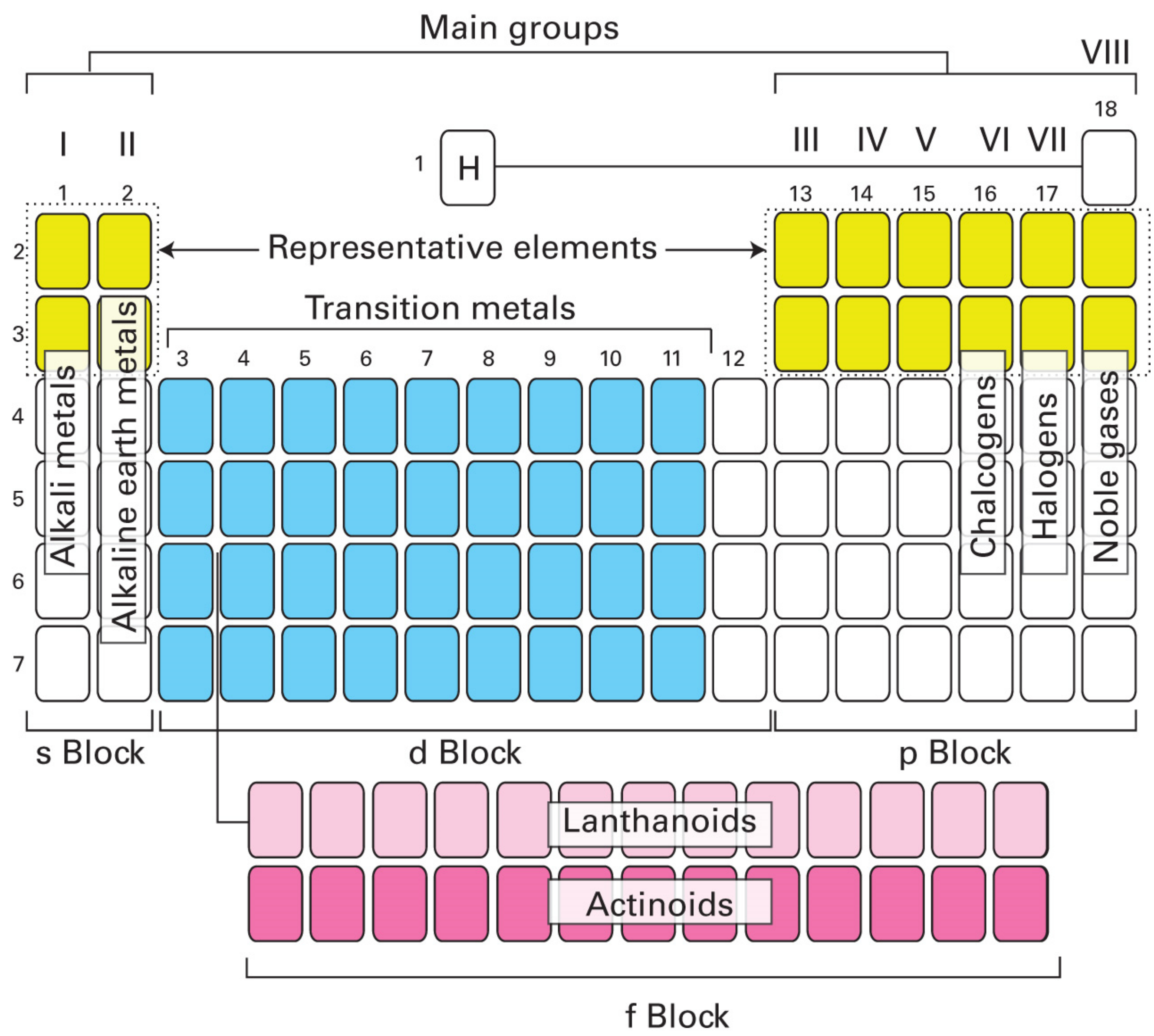
Lewis Structures;

Oxidation States;

Formal Charges

Inorganic Chemistry Chapter 1: Figure 1.22

W. H. FREEMAN



Trends in Atomic Properties

- Size (atomic, ionic, covalent, van der Waals radii)
- Ionization Potential ($A^0_{(g)}$ + I.E. $\longrightarrow$ A^+ + e^-)
- Electron Affinity Energies ($A^0_{(g)}$ + e^- $\rightarrow$ A^- + E.A.E.)
- Electronegativity: Ability of an atom, within a molecule to attract electrons to itself.

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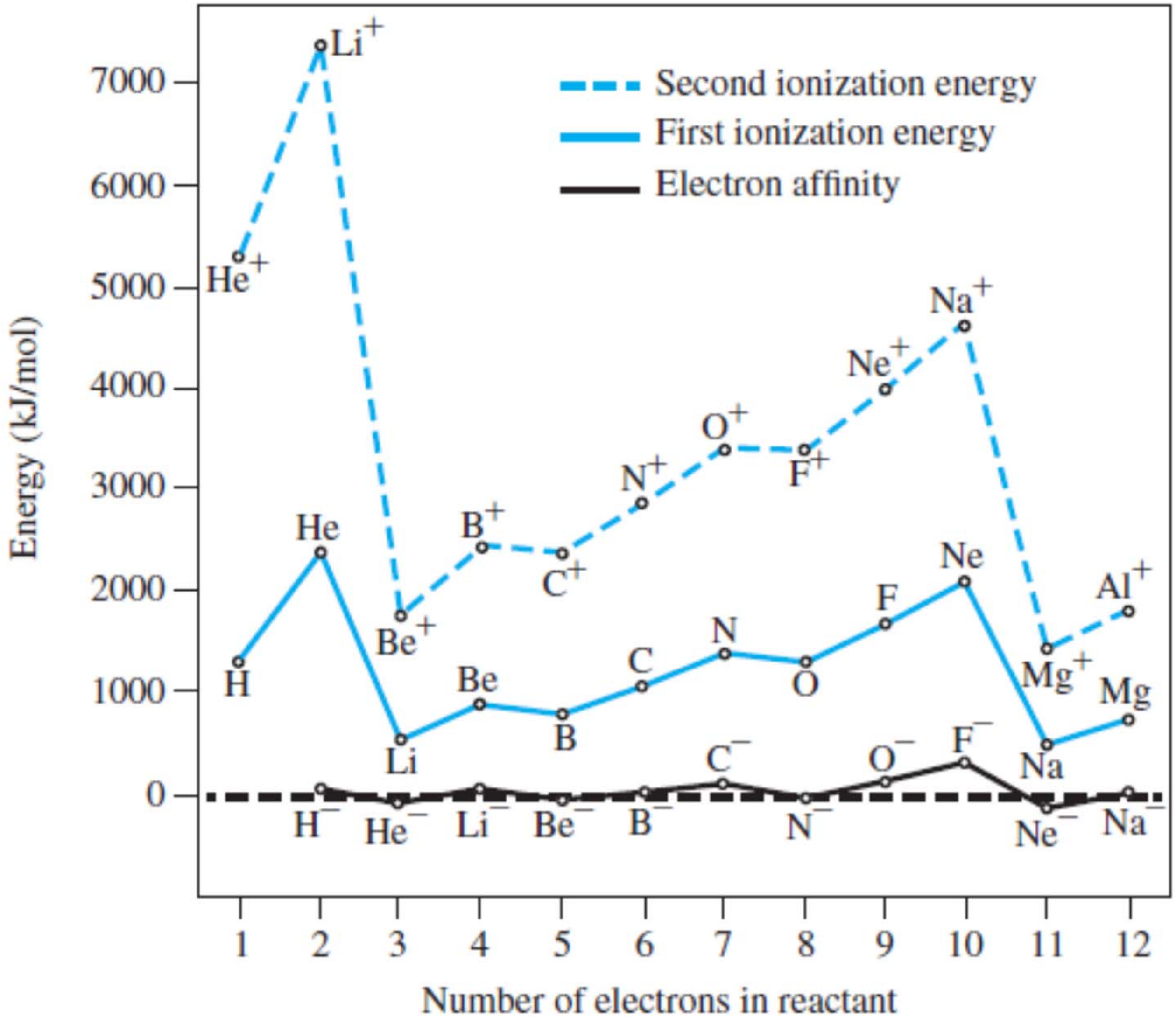
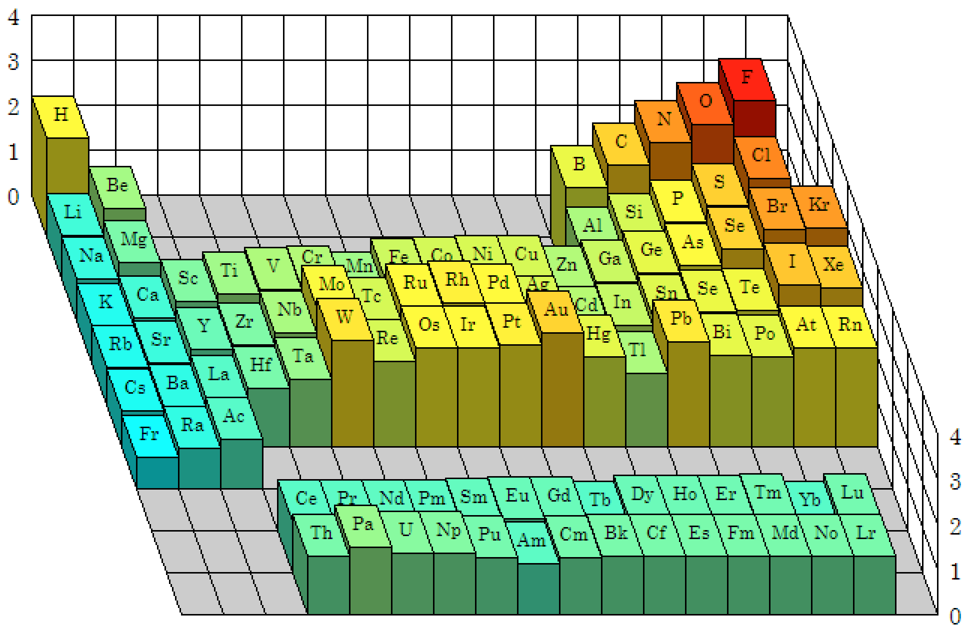

Second ionization energy
First ionization energy
Electron affinity
Energy (kJ/mol)
7000
6000
5000
4000
3000
2000
1000
0
Li+
He+
Na+
Ne+
O+
F+
N+
B+
C+
Be+
Al+
Mg+
He
H
Li
Be
B
C
N
O
F
Ne
Na
Mg
H−
He−
Li−
Be−
B−
C−
N−
O−
F−
Ne−
Na−
1
2
3
4
5
6
7
8
9
10
11
12
Number of electrons in reactant

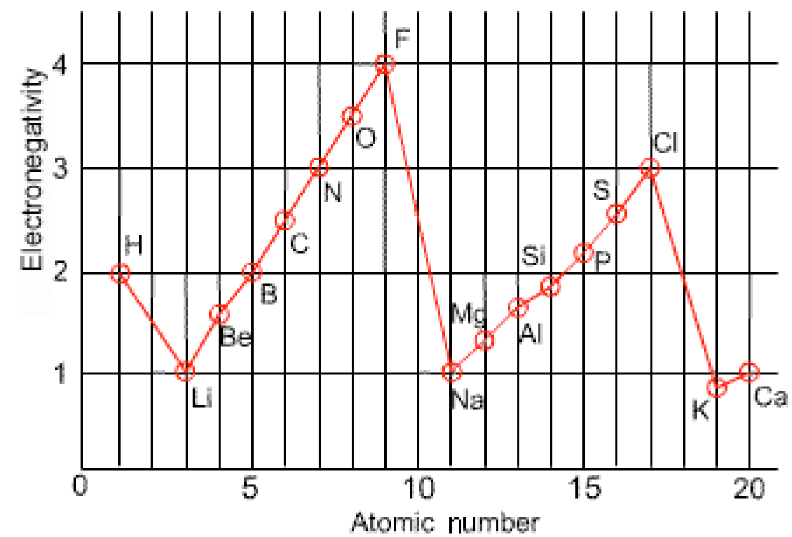
Table 1.6 First electron affinities of the main-group elements, E_a/(kJ mol^{-1})*

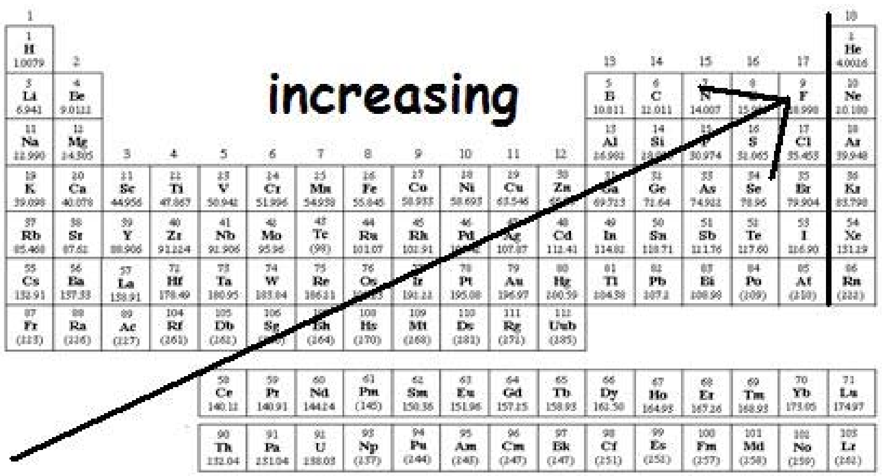
H							**He**
72							−48
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
60	≤ 0	27	122	−8	141	328	−116
					−780		
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
53	≤ 0	43	134	72	200	349	−96
					−492		
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
48	2	29	116	78	195	325	−96
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
47	5	29	116	103	190	295	−77

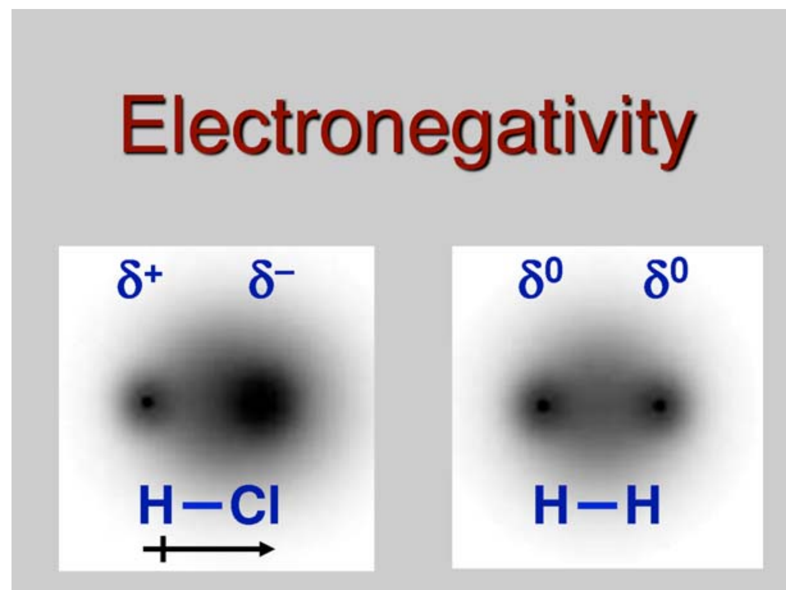
* The first values refer to the formation of the ion X^- from the neutral atom; the second value to the formation of X^{2-} from X^-.



Electronegativity







BDE: 427 436 kJ/mol

Electronegativity-

- Pauling

$$|\chi_A - \chi_B| = 0.208\sqrt{E_{A\text{-}B} - 1/2(E_{A\text{-}A} + E_{B\text{-}B})}$$

arithmetic mean

$$|\chi_A - \chi_B| = 0.208\sqrt{E_{A\text{-}B} - (E_{A\text{-}A} \cdot E_{B\text{-}B})^{1/2}}$$

geometric mean

- Mulliken

$$\chi_m = \frac{1}{2}(I + E_{ea})$$

- Rochow

Allred and Rochow Scale

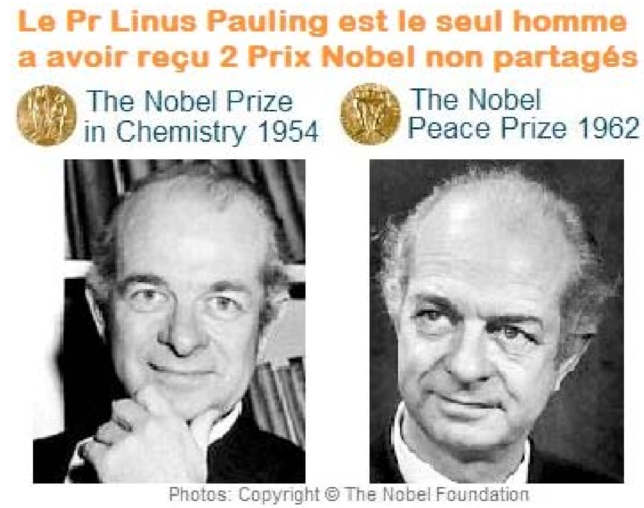
This scale considers electronegativity as the force acting on electrons at a distance of the covalent radius.

$$\chi = 0.744 + \frac{0.359\, Z_{eff}}{r_{cov}^2}$$

Z_{eff} = Effective nuclear charge

r_{cov} = Covalent radius of the atom in Angstroms.

Linus Pauling



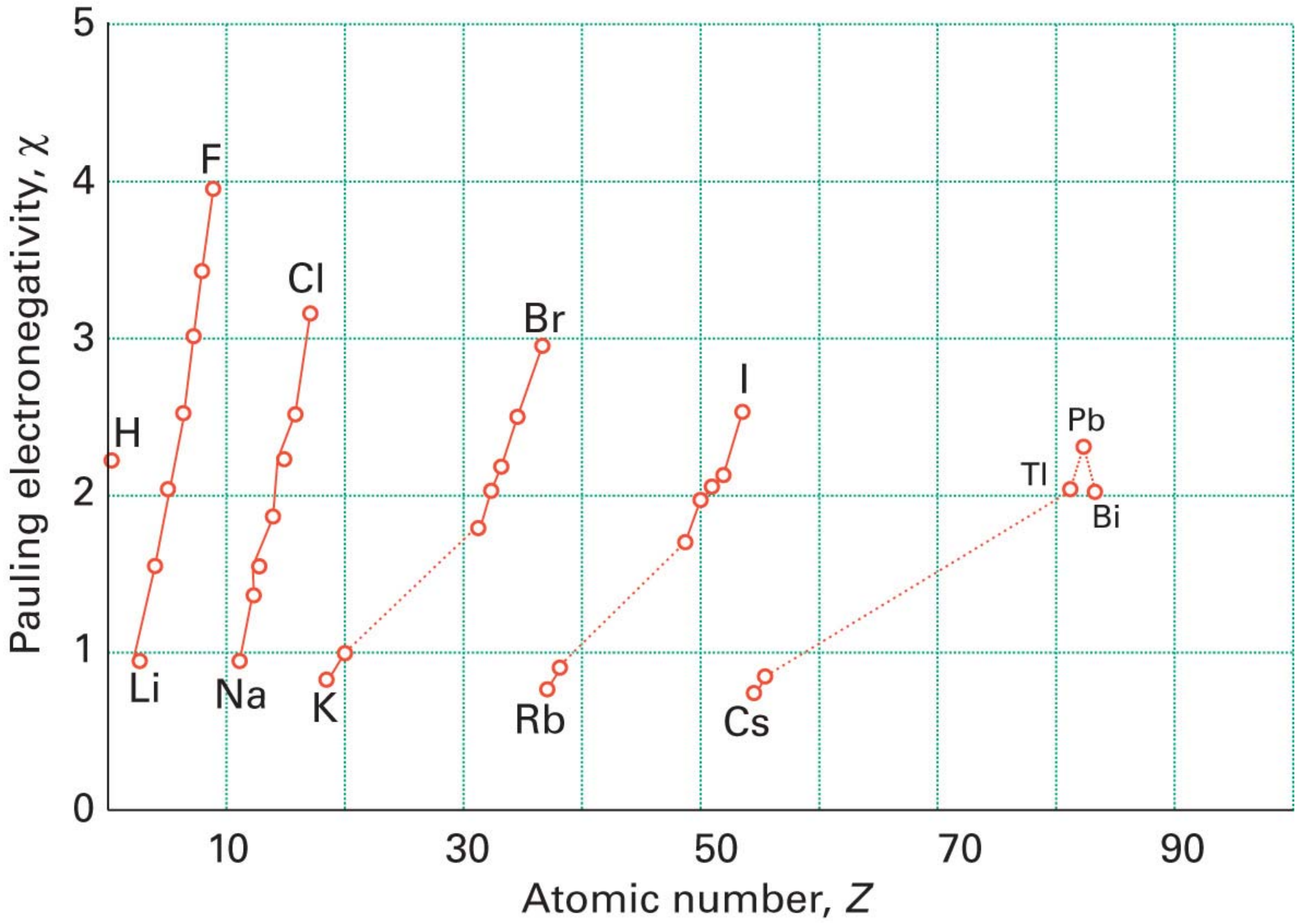
BDE H_2 = 436 kJ/mol
BDE Cl_2 = 239
BDE HCl = 427

Pauling: If strictly covalent: BDE HCl should be average of H_2 and Cl_2

Which would be ½ (436 + 239) = 338 kJ/mol. The extra stability is
Due to electronegativity difference, and electrostatic attraction. That is, this
Bond is polar covalent.

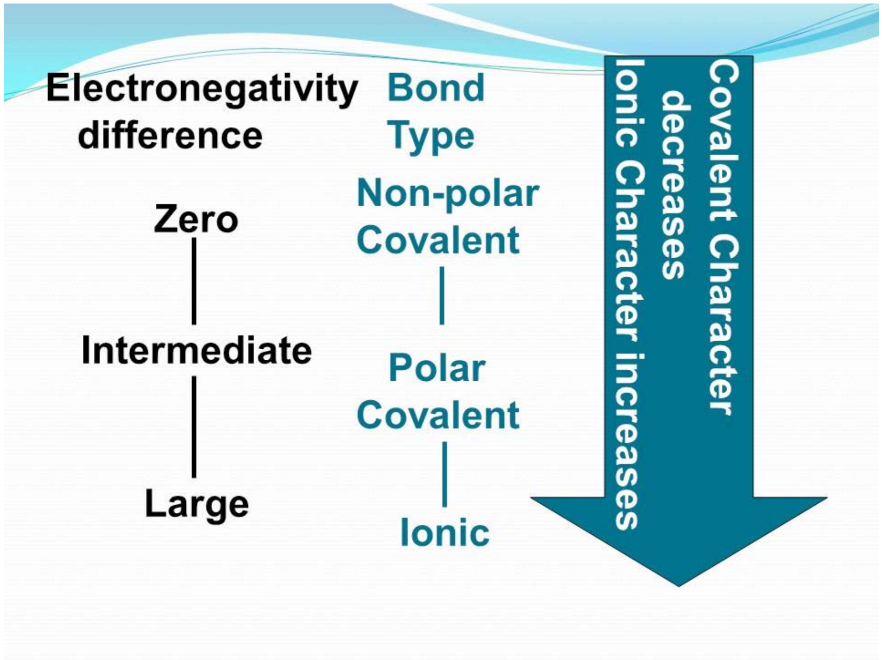
Table 1.7 Pauling χ_P, Mulliken, χ_M, and Allred–Rochow, χ_{AR}, electronegativities

H							**He**
2.20							5.5
3.06							
2.20							
Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
0.98	1.57	2.04	2.55	3.04	3.44	3.98	
1.28	1.99	1.83	2.67	3.08	3.22	4.43	4.60
0.97	1.47	2.01	2.50	3.07	3.50	4.10	5.10
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
0.93	1.31	1.61	1.90	2.19	2.58	3.16	
1.21	1.63	1.37	2.03	2.39	2.65	3.54	3.36
1.01	1.23	1.47	1.74	2.06	2.44	2.83	3.30
K	**Ca**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
0.82	1.00	1.81	2.01	2.18	2.55	2.96	3.0
1.03	1.30	1.34	1.95	2.26	2.51	3.24	2.98
0.91	1.04	1.82	2.02	2.20	2.48	2.74	3.10
Rb	**Sr**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
0.82	0.95	1.78	1.96	2.05	2.10	2.66	2.6
0.99	1.21	1.30	1.83	2.06	2.34	2.88	2.59
0.89	0.99	1.49	1.72	1.82	2.01	2.21	2.40
Cs	**Ba**	**Tl**	**Pb**	**Bi**			
0.79	0.89	2.04	2.33	2.02			
0.70	0.90	1.80	1.90	1.90			
0.86	0.97	1.44	1.55	1.67			



Pauling electronegativity, χ
Atomic number, Z
0
1
2
3
4
5
10
30
50
70
90
H
Li
F
Na
Cl
K
Br
Rb
I
Cs
Tl
Pb
Bi

Significance: Bond type



en= electronegativity

en > 1.7 = ionic bond

en < 1.7 = Polar covalent bond

en = 0
is non-polar covalent bond

Properties of Hydrogen Halides: polar covalent bonds, bond dipoles, electric dipole moments,

$\mu = q \times r$

Hydrogen Fluoride (HF)

m.p. -83.1°C, b.p. 19.9°C

pKa (aq) 3.17

r(H-F) = 0.92 Å; dipole moment = 1.8D

Hydrogen Chloride (HCl)

m.p. -114.2°C, b.p. -85.0 deg.C

pKa (aq) -7

r(H-Cl) = 1.28 Å; dipole moment = 1.1D

Hydrogen Bromide (HBr)

m.p. -86.8°C, b.p. -66.7°C

pKa (aq) -9

r(H-Br) = 1.41 Å; dipole moment = 0.8D

Hydrogen Iodide (HI)

m.p. -50.8°C, b.p. -35.35°C

pKa (aq) -10

r(H-I) = 1.60 Å; dipole moment = 0.4D

Why??? Electric dipole moment is the product of magnitude of charges and the distance of separation between the charges. Magnitude of charges will depend on difference in electronegativity of the atoms. Now in this case, F has highest electronegativity hence HF will have highest magnitude of charges. But, as we go down the group, the atomic radii increases, hence the distance of separation (bond length) will increase. So, we would expect the two factors to balance each other. Here, it seems the difference in electro-negativity out weighs the distance (bond length) and that is why Dipole moment decreases,

Covalent bond types

- Polar molecules
  - Electrons are not equally shared
  - One part of molecule is more negative than the another part of the molecule
  - Molecule thus has negative and positive 'poles' like a battery
  - Hydrophilic ('water loving')
- Nonpolar molecules
  - Electrons are equally shared
  - No one part of molecule is distinctly negative or positive; no 'poles'
  - Hydrophobic 'water fearing'

Water, a polar molecule

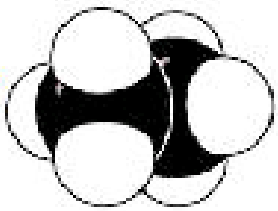
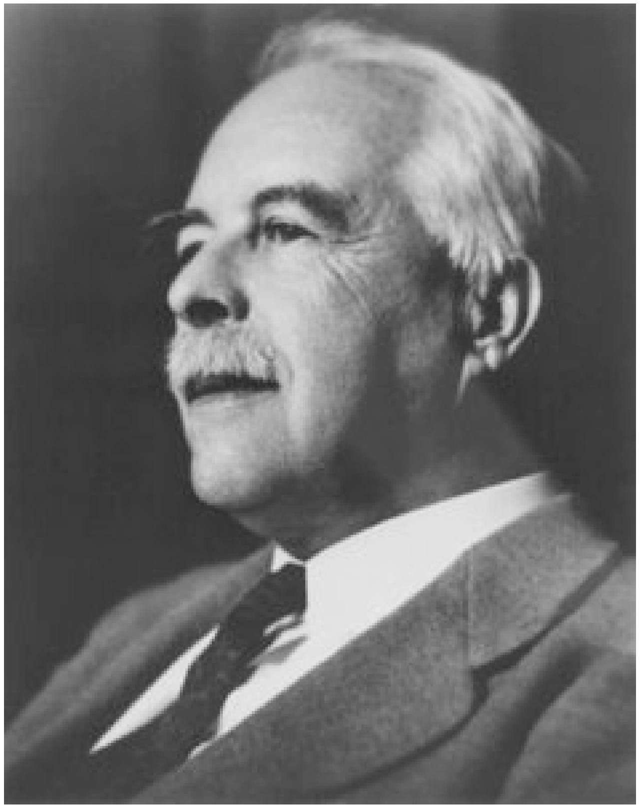

Ethane, a nonpolar molecule

Figure 1
Potential Energy Changes that Accompany Changes in the Internuclear Separation of Two Hydrogen Atoms

Two Electrons Shared between Two Atoms
Make a Bond!   G.N. Lewis

(G. = Gilbert
N. = Newton
Lewis as in Lewis Structures!)



Lewis Structures and VSEPR:

Workshop Study

Simple Review videos

https://www.youtube.com/watch?v=1ZlnzyHahvo
https://www.youtube.com/watch?v=xNYiB_2u8J4