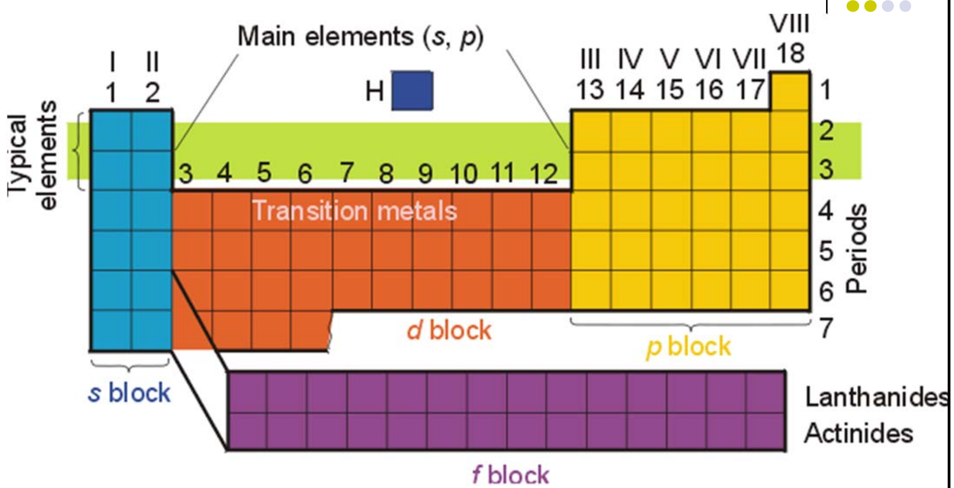
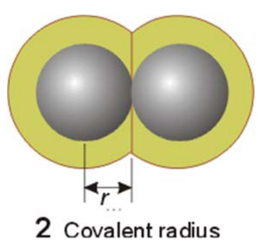
Periodic Trends



Generally, atoms with same outer-orbital structure appear in the same Column.

Effective atomic radius (covalent radius)



effective atomic radius
=1/2(d_{AA} in the molecule A_2)

Example:

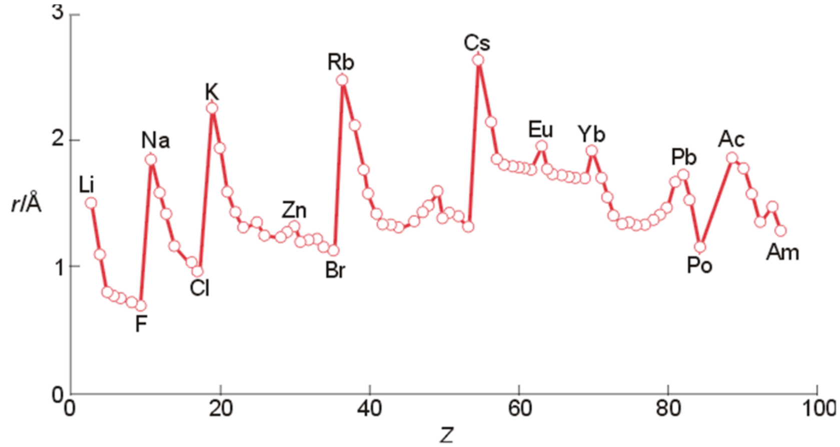
H_2: d=0.74 Å → r_H=0.37 Å

Estimating bond distance (covalent):

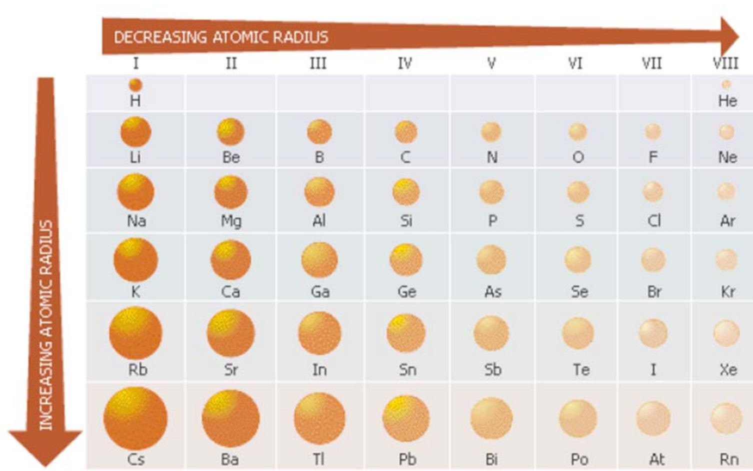
R----C-H: $d_{C-H} = r_C + r_H$ =0.77 + 0.37 =1.14 Å

Trend 1. Atomic radii increase down a group (Z_{eff} ~constant while n increases).

Trend 2: Atomic radii decrease across a period (Z_{eff} increase)



Atomic Radii



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Na $1s^2 2s^2 2p^6 3s^1$

$$Z_{eff} = 11 - 8 \times 0.85 - 2 = 2.2$$

K $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

Rb $Z_{eff}=2.2$

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	Na	Mg	Al	Si	P	S	Cl
[Ne]	$3s^1$	$3s^2$	$3s^2 3p^1$	$3s^2 3p^2$	$3s^2 3p^3$	$3s^2 3p^4$	$3s^2 3p^5$
Z	11	12	13	14	15	16	17
σ	8.8	9.15	9.5	9.85	10.2	10.55	10.9
Z_{eff}	2.2	2.85	3.5	4.15	4.8	5.45	6.1

$\Delta Z = 1$

$\Delta \sigma = 0.35$

$\Delta Z_{eff} = 0.65$

Ionization energy:
Energy required to remove an electron from a gaseous atom or ion.

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \Delta E = IE_1$$

$$A^{+}(g) \rightarrow A^{2+}(g) + e^{-} \qquad \Delta E = IE_2$$

Trend 1: IE_1 decrease down a group(n, r increase while Z_{eff} constant).

Trend 2: IE_1 increases across a period (Z_{eff} increase, r decrease)

Exception: B, O ionization energy lower than Be, N: empty or half filled orbitals contribute to the stability.
Similarly: Al, S

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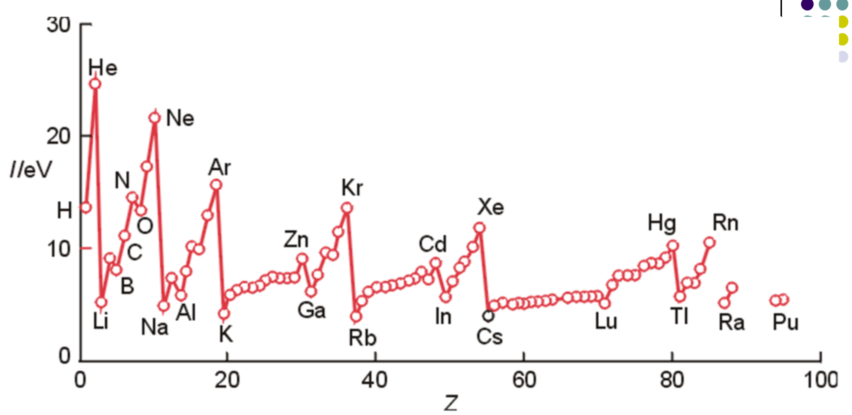
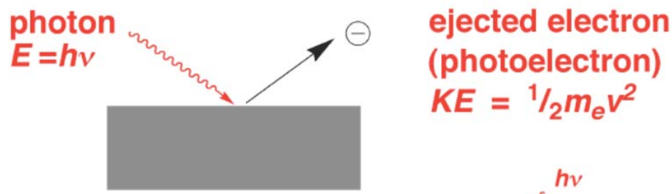


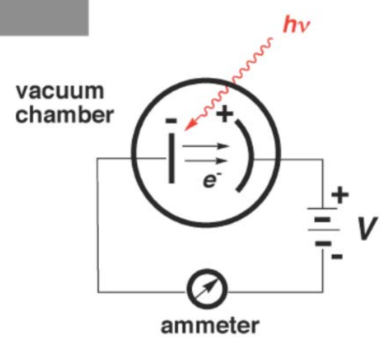
$$B^{+}: 1s^2 2s^2$$

$$O^{+}: 1s^2 2s^2 2p^3$$

Measurement of Ionization Energies: Einstein and the Photoelectric Effect

Einstein's photoelectric law: $h\nu = IE + \frac{1}{2}m_e v^2$





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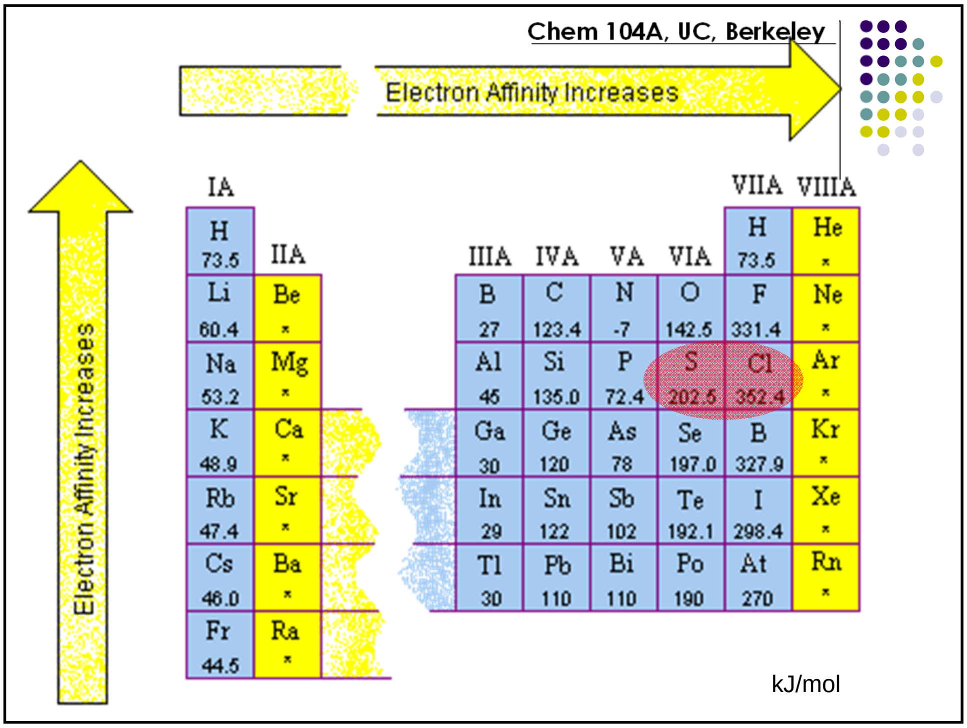
Electron affinity= energy required to remove an electron from the gaseous negative ion (<u>ionization energy of anion</u>).

$$A^-(g) \rightarrow A\ (g) + e^-$$

$$\Delta E = EA$$

- **maximum for halogens**
- **usually positive, difficult to measure, but can be negative.**
- **EA(F) lower than EA(Cl):**
  smaller diameter, strong e-e repulsion



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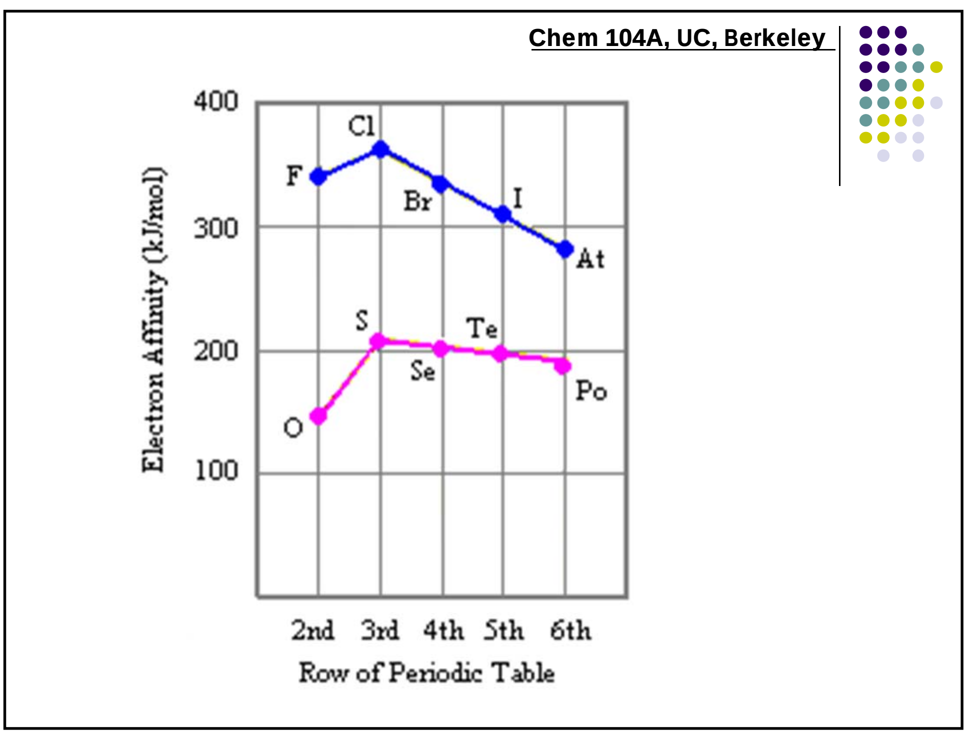
Electron Affinity Increases
Electron Affinity Increases
IA
IIA
IIIA IVA VA VIA
VIIA VIIIA
H 73.5
Li 60.4
Be *
Na 53.2
Mg *
K 48.9
Ca *
Rb 47.4
Sr *
Cs 46.0
Ba *
Fr 44.5
Ra *
B 27
C 123.4
N -7
O 142.5
F 331.4
Al 45
Si 135.0
P 72.4
S 202.5
Cl 352.4
Ga 30
Ge 120
As 78
Se 197.0
B 327.9
In 29
Sn 122
Sb 102
Te 192.1
I 298.4
Tl 30
Pb 110
Bi 110
Po 190
At 270
H 73.5
He *
Ne *
Ar *
Kr *
Xe *
Rn *
kJ/mol



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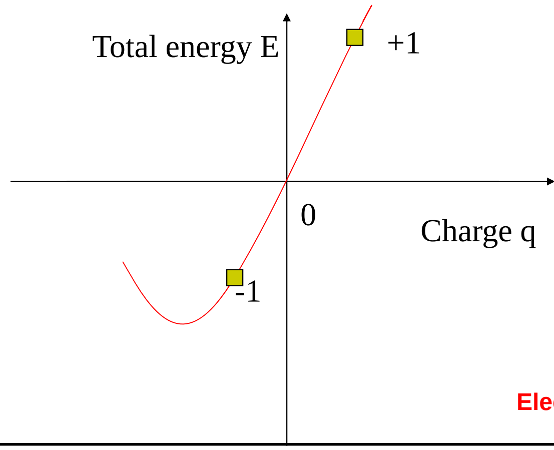
Electron Affinity (kJ/mol)
400
300
200
100
F
Cl
Br
I
At
O
S
Se
Te
Po
2nd 3rd 4th 5th 6th
Row of Periodic Table

Total energies of an ion in various charge states:

$E=\alpha q+\beta q^2$ (q =ionic charge)

The slope of this curve near the origin gives us an idea of how readily the atom accepts and gives up electrons.



Electronegativity (EN)

Electronegativity (EN)

The power of an atom in a molecule to attract electrons to itself

Mulliken definition: EN =1/2(IE_1+EA)

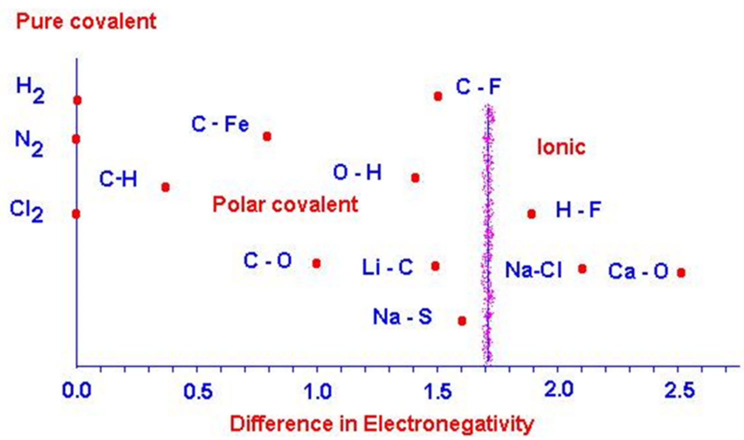
Pauling definition:

$$EN_A - EN_B = 0.208\sqrt{DE_{AB} - \sqrt{DE_{A^2}DE_{B^2}}}$$

EN(F)=3.98

DE =bond dissociation energy in kcal/mol

EN(A) –EN(B) small → A-B bonding mostly covalent
EN(A)-EN(B) large → A-B bonding has ionic component



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Example:

HF

DE (H_2) =103 kcal/mol
DE(F_2) =37 kcal/mol
DE(HF)=135 kcal/mol

$$\sqrt{DE_{H2}DE_{F2}} = 62 kcal/mol$$

EN(F)-EN(H) = $0.208\sqrt{135-62} = 1.78$

EN(H) =2.2

Trend 1. EN decrease down a group
Trend 2: EN increase across a period

H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 2.00	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Te 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66
Cs 0.79	Ba 0.89	La 1.10	Hf 1.30	Ta 1.50	W 2.36	Re 1.90	Os 2.20	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02	Po 2.00	At 2.20