2.Ionization Energies

Ionization energy, IE, is the energy required to remove one electron from an atom or ion;
an **endothermic** process

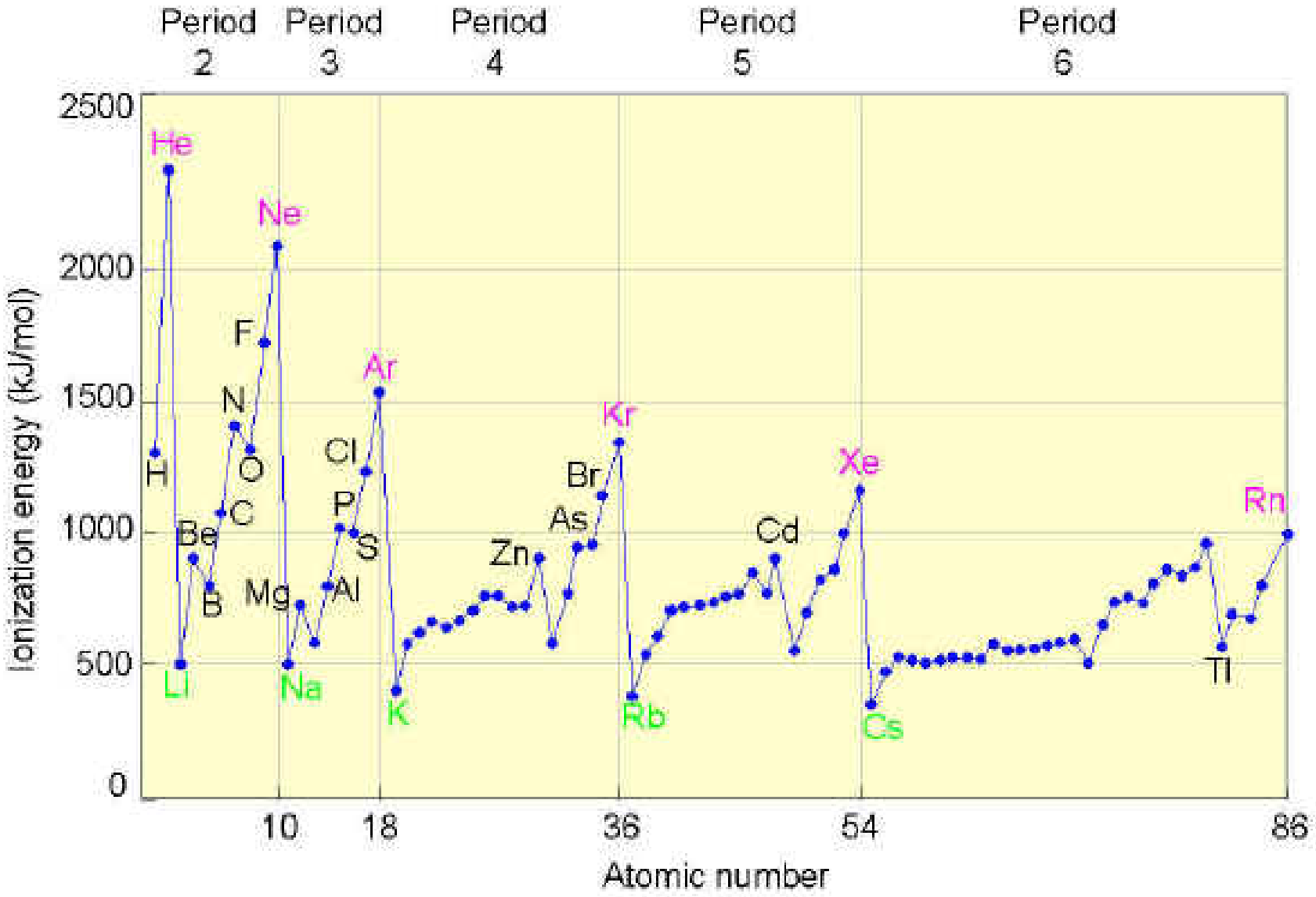
that is, $A \rightarrow A^+ + 1\ e^-$ $\Delta H = +ve$

The energy, in kJ mol^{-1}, required to remove 1 electron from the neutral atom (1^{st} ionization limit) depends on the orbital in which the electron resides

Two general trends:

1.) IEs **decrease down a group**
(an electron removed from an orbital more distant from the nucleus is less tightly bound)

2.) IEs **increase from left to right** across a period
(electrons being removed from orbitals of equal n are subject to increasing nuclear attraction)


Period 2
Period 3
Period 4
Period 5
Period 6
2500
2000
1500
1000
500
0
Ionization energy (kJ/mol)
He
Ne
Ar
Kr
Xe
Rn
H
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
Cl
K
Zn
As
Br
Rb
Cd
Cs
Tl
10
18
36
54
86
Atomic number

Properties

There are some exceptions to generality 2).

They occur whenever the removal of $1e^-$ leads to a filled or half-filled orbital.

The extra stability of filled or half-filled orbitals leads to a lower IE for those elements which are one electron away from such a state

Example: IE of B < Be

B ≡ $1s^2 2s^2 2p^1$ Be ≡ $1s^2 2s^2$

$2p^1$ electron more easily lost than 1 electron from the filled 2s orbital

Example: IE O < N

O ≡ $1s^2 2s^2 2p^4$ N ≡ $1s^2 2s^2 2p^3$

By losing $1e^-$ O attains half-filled 2p-orbitals

Electron Affinities

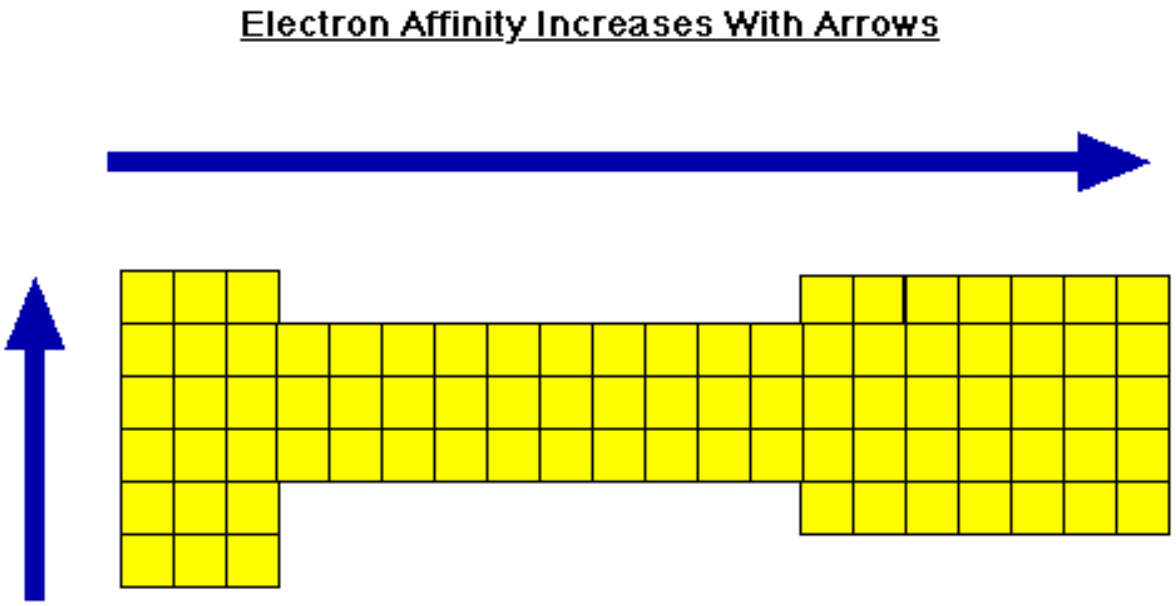
Electron affinity, EA, is the energy change that results from the **capture of an electron** by a neutral atom

that is, $A + e^- \rightarrow A^-$ EA (=ΔH which can +ve or -ve)

Again there are two general trends:

1.) EAs decrease down a group
(because e^-s are being captured in orbitals more distant from the nucleus)

2.) EAs increase across a period
(because e^-s are being captured in orbitals exposed to a greater nuclear charge)



EAs are especially large (large and –ve) when capture of an e^- leads to filled or half-filled orbitals.

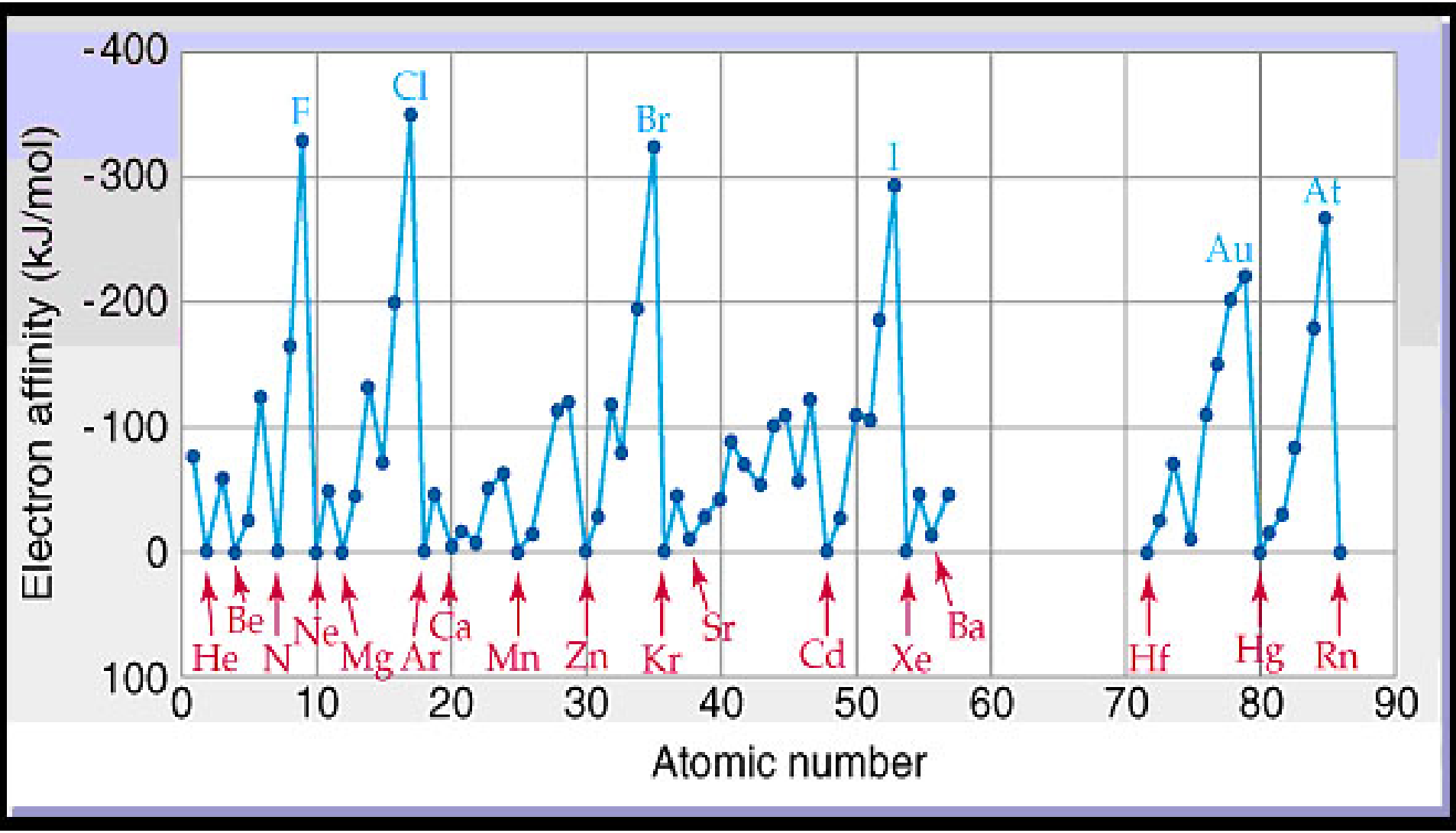
Example: $C + e^- \rightarrow C^-$

$C \equiv 1s^2 2s^2 2p^2$ $C^- \equiv 1s^2 2s^2 2p^3$

EAs tend to be important for non-metallic elements where their anions play an important role in their chemistry”

These elements include H and those of groups 16 and 17, where their valence shells are nearly full, and adding one or two electrons will make them “rare gas”-like; that is, a filled octet.

H	F	Cl	Br	I	
-73	-328	-349	-329	-295	$kJmol^{-1}$


Electron affinity (kJ/mol)
-400
-300
-200
-100
0
100
0
10
20
30
40
50
60
70
80
90
Atomic number
F
Cl
Br
I
Au
At
He
Be
N
Ne
Mg
Ar
Ca
Mn
Zn
Kr
Sr
Cd
Xe
Ba
Hf
Hg
Rn

Electronegativity

Electronegativity is the tendency of an atom in a covalently bonded molecule to attract the bonding electron pair to itself

It follows the same trend as electron affinity;

that is, it increases going up a group and across a period.

Values are relative and not absolute

The greatest electronegativity values are found with small non-metals.

F is the most electronegative element.

Electronegativity is important in bonding because a bond between two atoms of different electronegativity is polarized, with the e^- pair closer to the more electronegative atom

For example:

We write: $H^{\delta+}$ - $Cl^{\delta-}$ to denote that Cl is more electronegative than hydrogen.

Because electronegativity is a relative concept, there have been many attempts to place each element on a scale using different criteria.

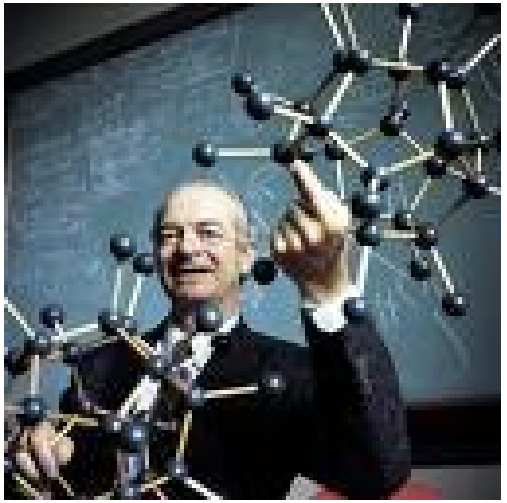
The most common scale is due to Linus Pauling which is based on the balance between IPs and EAs.

The electronegativities of some important non-metallic elements are (and these need not be memorized):

$$F > O > Cl > N \approx Br > I > S > Se > C > H \approx P$$

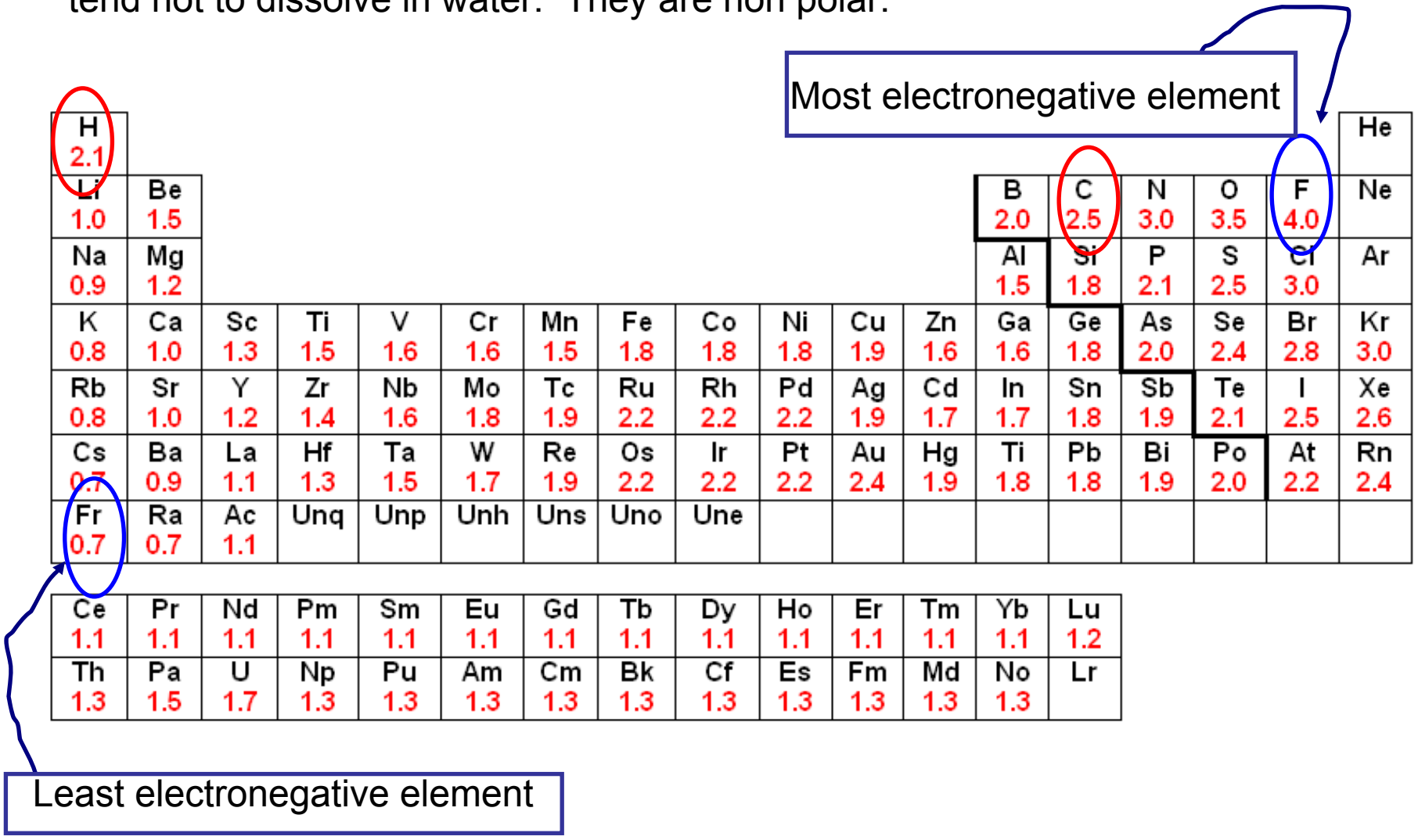
Note: C and H are not that electronegative so CH compounds are relatively non polar.

Who was Pauling?



- Linus Pauling was an American chemist.
- He was born in 1901and died 1994
- Won the Nobel Prize in Chemistry in 1954 for his work on the theory of the chemical bond, and the Nobel Peace Prize in 1962 for his campaign against above-ground nuclear testing
- Best known in his last years as a strong advocate for the consumption of massive amounts of Vitamin C for health

Note: electronegativity of H and C are similar. This is why organic hydrocarbon tend not to dissolve in water. They are non polar.



H 2.1																He
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar
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 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
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	Xe 2.6
Cs 0.7	Ba 0.9	La 1.1	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	Ti 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn 2.4
Fr 0.7	Ra 0.7	Ac 1.1	Unq	Unp	Unh	Uns	Uno	Une									

Ce 1.1	Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.1	Lu 1.2
Th 1.3	Pa 1.5	U 1.7	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr