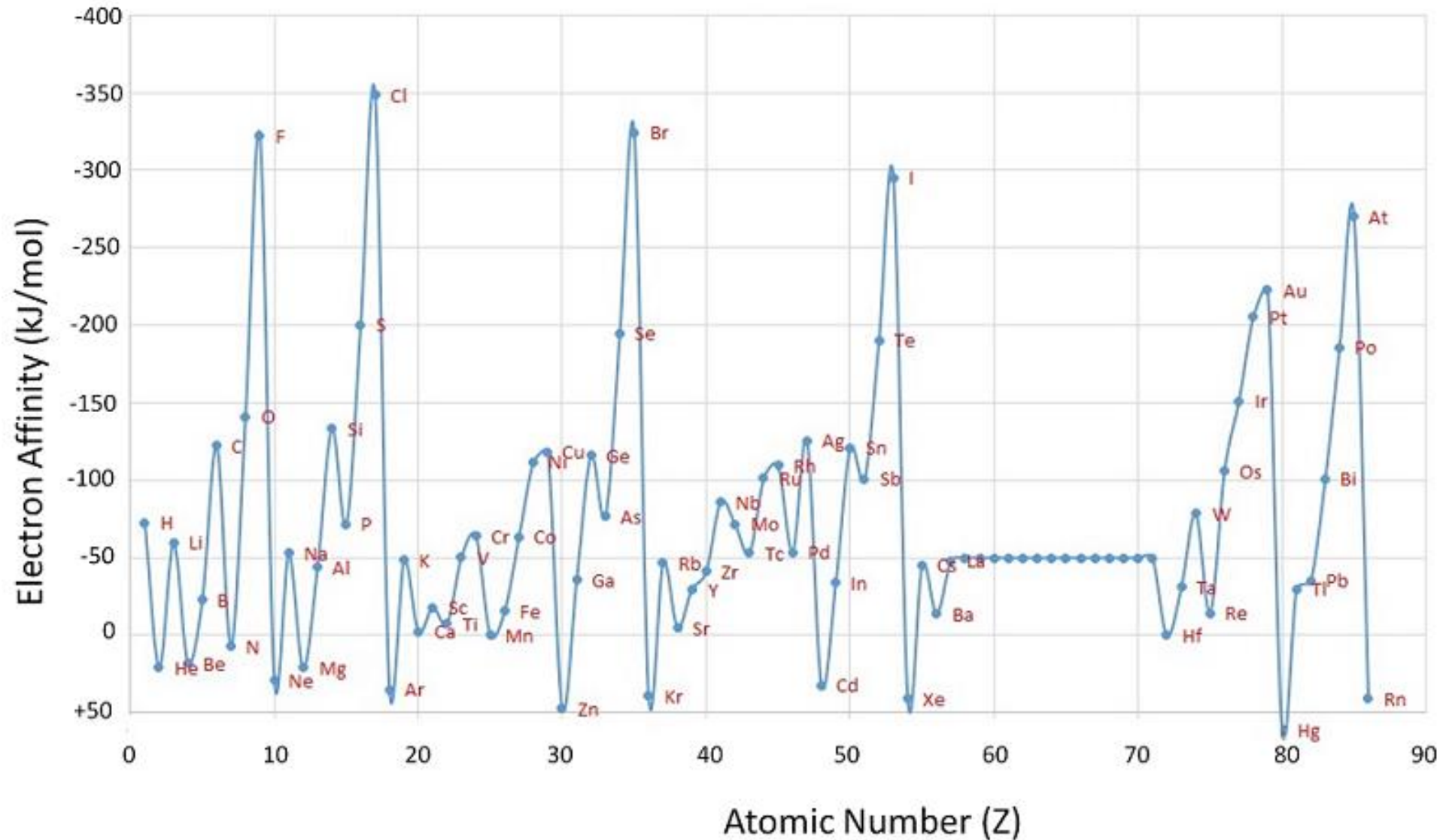
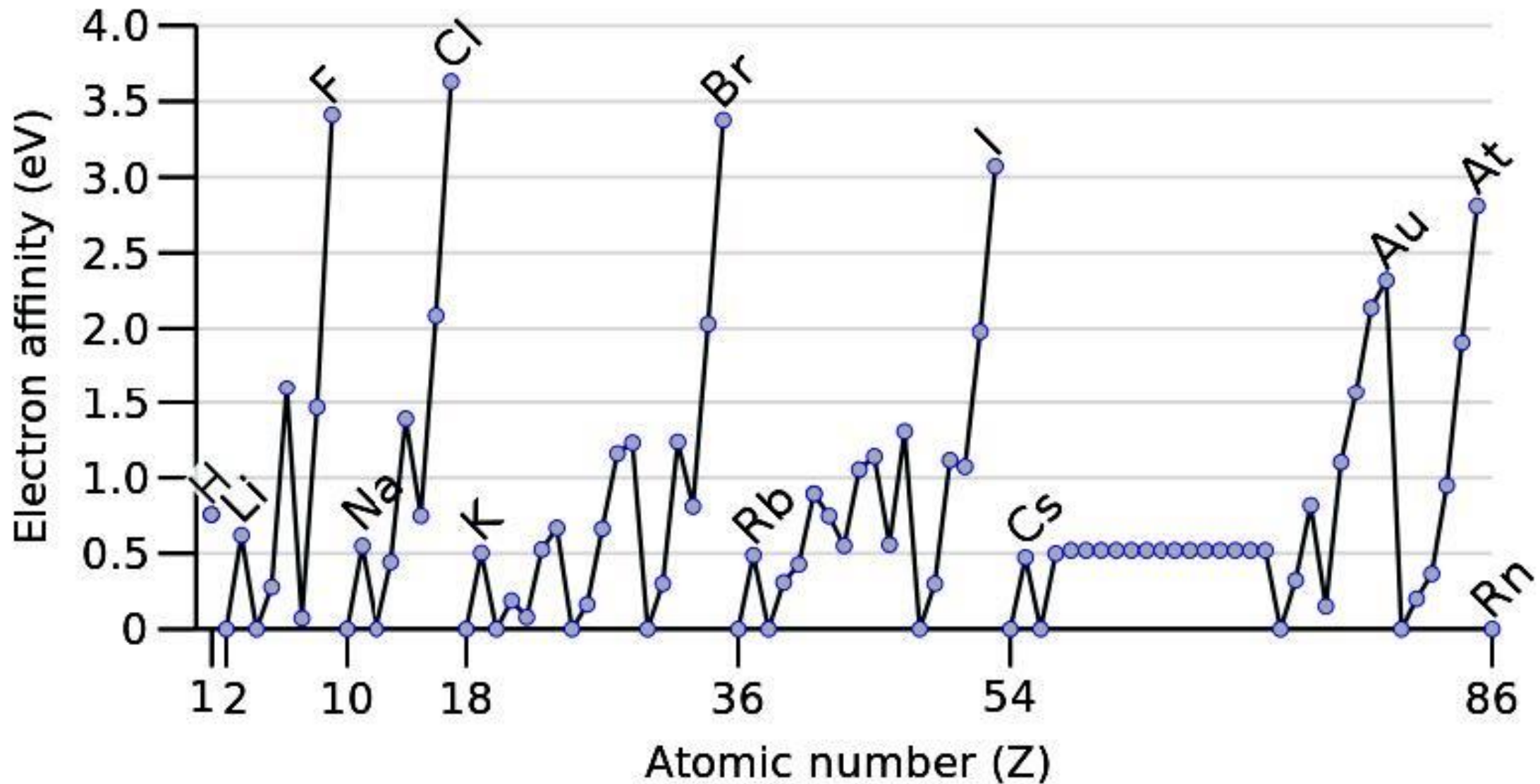


## Periodic variation of electron affinity:

Electron affinity is defined as the change in energy (in kJ/mole) of a neutral atom (in the gaseous phase) when an electron is added to the atom to form a negative ion. In other words, the neutral atom's likelihood of gaining an electron.



In eV unit:



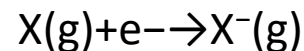
Energy of an atom is defined when the atom loses or gains energy through chemical reactions that cause the loss or gain of electrons. A chemical reaction that releases energy is called an exothermic reaction and a chemical reaction that absorbs energy is called an endothermic reaction.

Energy from an exothermic reaction is negative, thus energy is given a negative sign; whereas, energy from an endothermic reaction is positive and energy is given a positive sign.

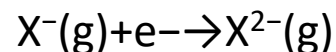
An example that demonstrates both processes is when a person drops a book. When he or she lifts a book, he or she gives potential energy to the book (energy absorbed). However, once the he or she drops the book, the potential energy converts itself to kinetic energy and comes in the form of sound once it hits the ground (energy released).

**Usually,** when an electron is added to a neutral atom (i.e., first electron affinity) energy is released; thus, the first electron affinities are negative. However, more energy is required to add an electron to a negative ion (i.e., second electron affinity) which overwhelms any the release of energy from the electron attachment process and hence, second electron affinities are positive.

First Electron Affinity (negative energy because energy released):



Second Electron Affinity (positive energy because energy needed is more than gained):



## First Electron Affinity

Ionization energies are always concerned with the formation of positive ions.

**Electron affinities are the negative ion equivalent, and their use is almost always confined to elements in groups 16 and 17 of the Periodic Table.**

The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous  $-1$  ions. It is the energy released (per mole of X) when this change happens. First electron affinities have negative values. For example, the first electron affinity of chlorine is  $-349 \text{ kJ mol}^{-1}$ . By convention, the negative sign shows a release of energy.

When an electron is added to a metal element, energy is needed to gain that electron (endothermic reaction). Metals have a less likely chance to gain electrons because it is easier to lose their valence electrons and form cations. It is easier to lose their valence electrons because metals' nuclei do not have a strong pull on their valence electrons. Thus, metals are known to have lower electron affinities.

Why is energy needed to do this? You are forcing an electron into an already negative ion. It's not going to go in willingly!



The positive sign shows that you have to put in energy to perform this change.

The second electron affinity of oxygen is particularly high because the electron is being forced into a small, very electron-dense space.

Electron Affinity Values for Selected Elements (kJ/mol)																			
Period	Group 1												Group 18						
1	H -72																		He +20*
2	Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30	
3	Na -53	Mg +230*											Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*	
4	K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*	
5	Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*	
6	Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*	
7	Fr	Ra																	

\* Calculated value

+30

This trend of lower electron affinities for metals is described by the Group 1 metals:

Lithium (Li): -60 KJ mol<sup>-1</sup>

Sodium (Na): -53 KJ mol<sup>-1</sup>

Potassium (K): -48 KJ mol<sup>-1</sup>

Rubidium (Rb): -47 KJ mol<sup>-1</sup>

Cesium (Cs): -46 KJ mol<sup>-1</sup>

**Notice that electron affinity decreases down the group.**

When moving down a group, the electron affinity generally decreases. This is because as you go down the period table, new valence shells are added increasing the atomic radius. The new orbital is further away from the nucleus, meaning the attraction between the positively charged nucleus and the new electron decrease. Thus, electron affinity decreases.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases.

We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups.

The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher  $n$  level, which is more difficult to do. Group 2 (2A) has a filled  $ns$  subshell, and so the next electron added goes into the higher energy  $np$ , so, again, the observed EA value is not as the trend would predict.

Finally, group 15 (5A) has a half-filled  $np$  subshell and the next electron must be paired with an existing  $np$  electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

Electron Affinity trend for Gr. 17:

Fluorine (F) =  $-328 \text{ kJ mol}^{-1}$   
Chlorine (Cl) =  $-349 \text{ kJ mol}^{-1}$   
Bromine (Br) =  $-324 \text{ kJ mol}^{-1}$   
Iodine (I) =  $-295 \text{ kJ mol}^{-1}$

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges.

However, as we move down a group, we see that the second element in the group most often has the greatest EA.

The reduction of the EA of the first member can be attributed to the small size of the  $n = 2$  shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of  $-348 \text{ kJ/mol}$ , has the highest value of any element in the periodic table. The EA of fluorine is  $-322 \text{ kJ/mol}$ . When we add an electron to a fluorine atom to form a fluoride anion ( $\text{F}^-$ ), we add an electron to the  $n = 2$  shell.

The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell.

The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the  $n = 3$  shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

### **Factors governing electron affinities:**

(i) Size of the species: If  $Z^*$  per electron at the periphery is more or less the same for different species (e.g. in a group of representative elements), the electrostatic interaction towards the nucleus experienced by the electrons at the periphery is less for the larger species. Here slight increasing trend of  $Z^*$  is less important than the effect of increasing trend of  $n$  (principal q.n.) when we move down from top to bottom.  $r \propto n^2$  and  $r \propto 1/Z^*$ .

For such systems, the accommodation of an additional electron which is to be bound at the periphery by the attractive force of the nucleus is disfavored more for larger species.

Thus, in general, smaller atom in a group possess higher energy.

(ii) The species with higher  $Z^*$  will have higher EA

(iii) Nature of the orbital. The orbitals which can better penetrate into the inner electron clouds are more suitable to house the incoming electron.  $ns > np > nd > nf$ , ease of accommodation order

(iv) Nature of the electronic configuration: half-filled, full-filled etc.



### Variation/Violation of E.A. in the periodic table:

(i) Gr. IIA (2) metals: Be, Mg, Ca etc. has  $ns^2$  orbital structure. Hence accommodation of an incoming electron makes it  $ns^2np^1$ . It is a disfavored process.

Thus Gr. IA metals have higher EA than Gr.IIA as in Gr. IA addition of an electron gives rise to  $ns^2$  configuration.

(i) Transition series:

Sc-0, Ti-20, V-50, Cr-64, Mn-0, Fe-24, Co-70, Ni-111, Cu-118, Zn-0 (KJ/mol)

Drop in Mn and Zn

(iii) Postlanthanides: Due to lanthanide contraction, among postlanthanides, the EA is usually high.

In a group:

1. Moving down the group size gradually increases, thus EA decreases.

$r$  is proportional to  $n^2/z^*$ . as  $n$  is square term so slight increasing effect of  $Z^*$  is becoming less significant.

Exceptions:  $F < Cl$ ,  $O < S$ ,  $N < P$ ,  $B < Al$ . Here added electron creates unfavorable effect.

In addition, the possibility of delocalization of the increased electron density in the vacant 3d orbital reduces the repulsions for the 3<sup>rd</sup> period of elements.

Thus the reduced e-e repulsions in the 3<sup>rd</sup> period elements outweigh the factor due to the large electrostatic attraction experienced in their corresponding 2<sup>nd</sup> period of elements.

2. Higher EA of the heavier congeners of the d-block elements: For the d- and f-block elements, due to contraction effect, the size does not increase smoothly.

Co (70) < Rh (120) < Ir (160)

Ni (111) < Pd (160) < Pt (205)

Cu (118) < Ag (126) < Au (223)

**Ionic aurides are now well-established ( $Cs^+Au^-$ )**

## Why is Fluorine an Anomaly?

The incoming electron is going to be closer to the nucleus in fluorine than in any other of these elements, so you would expect a high value of electron affinity. However, because fluorine is such a small atom, you are putting the new electron into a region of space already crowded with electrons and there is a significant amount of repulsion. This repulsion lessens the attraction the incoming electron feels and so lessens the electron affinity. A similar reversal of the expected trend happens between oxygen and sulfur in Group 16. The first electron affinity of oxygen ( $-142 \text{ kJ mol}^{-1}$ ) is smaller than that of sulfur ( $-200 \text{ kJ mol}^{-1}$ ) for exactly the same reason that fluorine's is smaller than chlorine's.

## Practice Problems

1. When an electron is added to a nonmetal atom, is energy released or absorbed?
2. Why do nonmetal atoms have a greater electron affinity than metal atoms?
3. Why are atoms with a low electron affinity more likely to lose electrons than gain electrons?
4. As you move down a group of the periodic table, does electron affinity increase or decrease, if so, why?
5. Why do nonmetals want to gain electrons?
6. Why do metals have a low electron affinity?

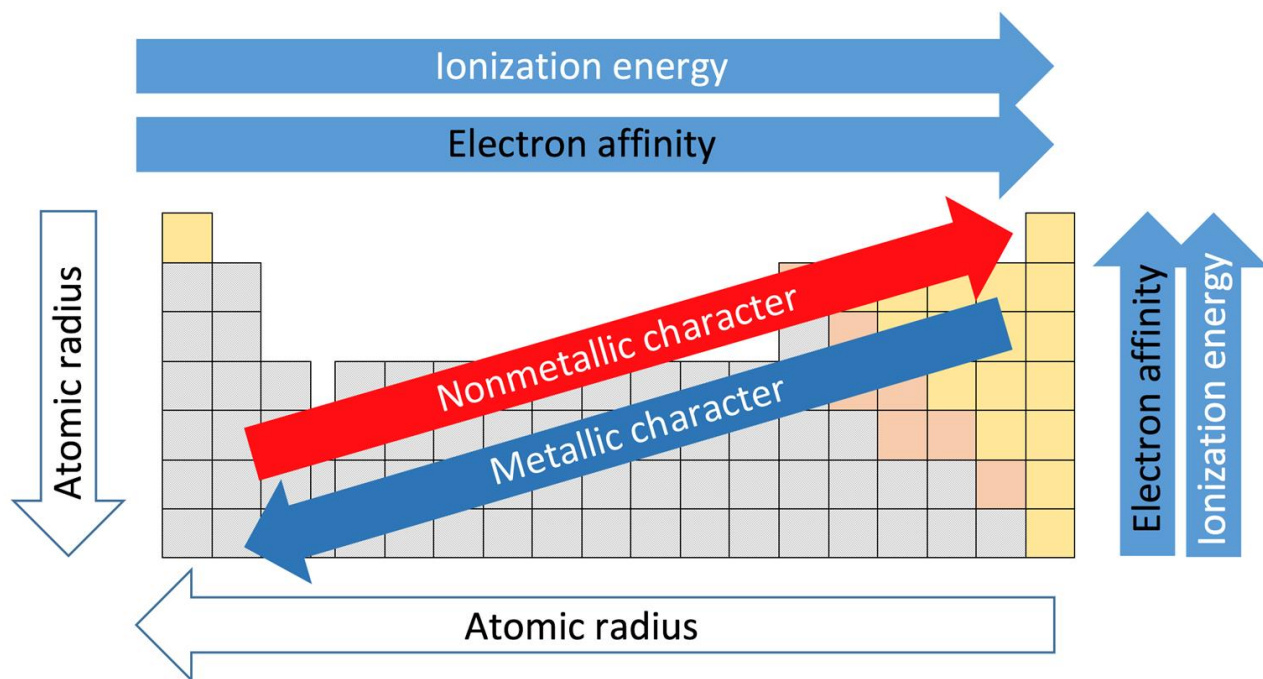
## Answers

1. Energy is released when a electron is added to a nonmetal.
2. Nonmetals have a greater electron affinity than metals because their atomic structure allows them to gain electrons rather than lose them.
3. Atoms with a low electron affinity want to give up their valence electrons because they are further from the nucleus; as a result, they do not have a strong pull on the valence electrons.
4. As you move down a group on the periodic table, electron affinity decreases. First, the electrons are placed in energy levels further away from the nucleus, which results in electrons not having a strong attraction to the nucleus; secondly, the atom does not want gain electrons because there is minimal charge on the outer energy levels from the nucleus; and lastly, the shielding effect increases, causing repulsion between the electrons, thus they move further from each other and the nucleus itself.
5. Nonmetals want to gain electrons because they have more valence electrons than metals, so it is easier for them to gain electrons than lose the valance electrons to fulfill a stable octet. In addition, nonmetals' valance electrons are closer to the nucleus, thus allowing more attraction between the two.
6. Metals have a low electron affinity (a less likely chance to gain electrons) because they want to give up their valence electrons rather than gain electrons, which require more energy than necessary. In addition, they do not have a strong pull on the valance electrons because they are far away from the nucleus, thus they have less energy for an attraction.

## Trends in Metallic and Nonmetallic Character

We have seen that metals are on the left side of the periodic table while nonmetals are generally on the right (exception: Hydrogen).

Metallic character has the opposite trend of ionization energy and electronegativity, but is similar to the trend we saw for atomic radius: it **INCREASES** as you move from right to left across rows of the periodic table and **INCREASES** as you move down columns. This trend does not necessarily apply to transition metals.

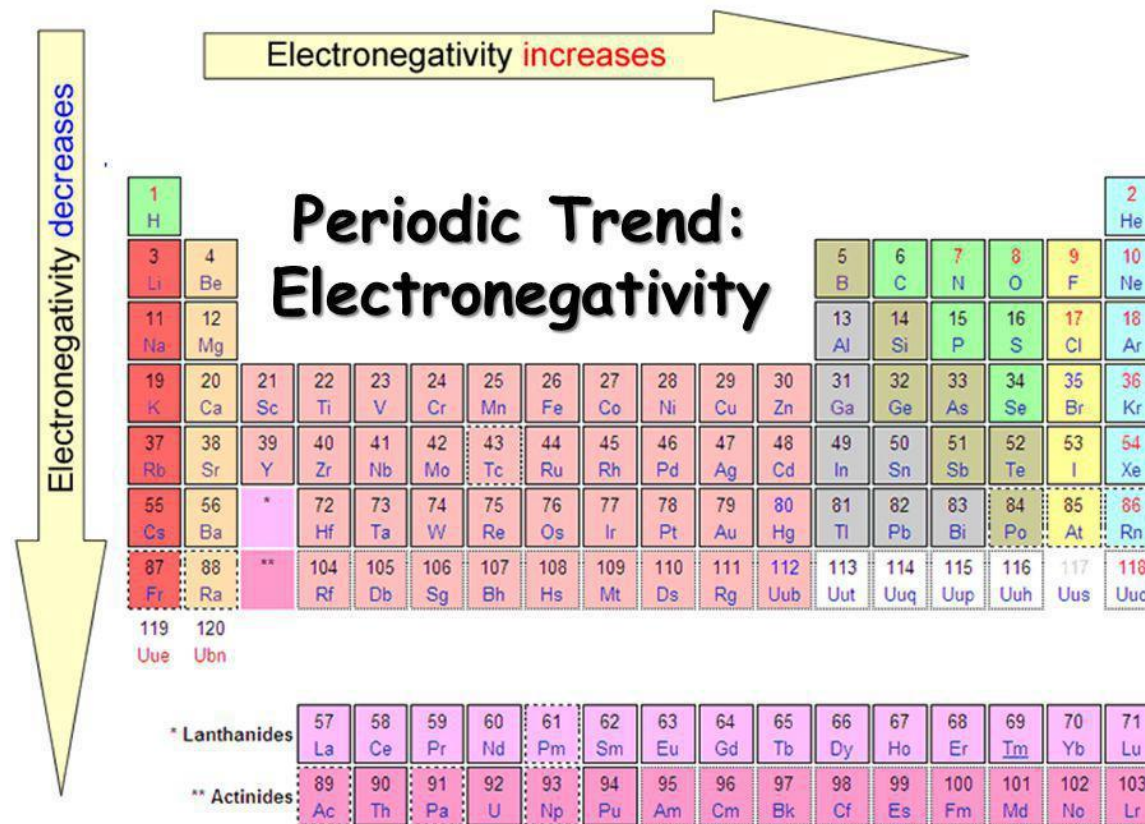


Metallic character increases as you go from right to left on periods and move down groups on the periodic table.

**The gray squares represent metals, the orange squares are "metalloids" and the yellow squares are nonmetals.**

Typical metalloids have a metallic appearance, but they are brittle and only fair conductors of electricity.

Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.



**Electronegativity, symbol  $\chi$ , is a chemical property that describes the ability of an atom to attract electrons towards itself in a covalent bond.**

- Electronegativity cannot be directly measured and must be calculated from other atomic or molecular properties. Several methods of calculation have been proposed and, although there may be small differences in the numerical values of the electronegativity, all methods show the same periodic trend between elements.

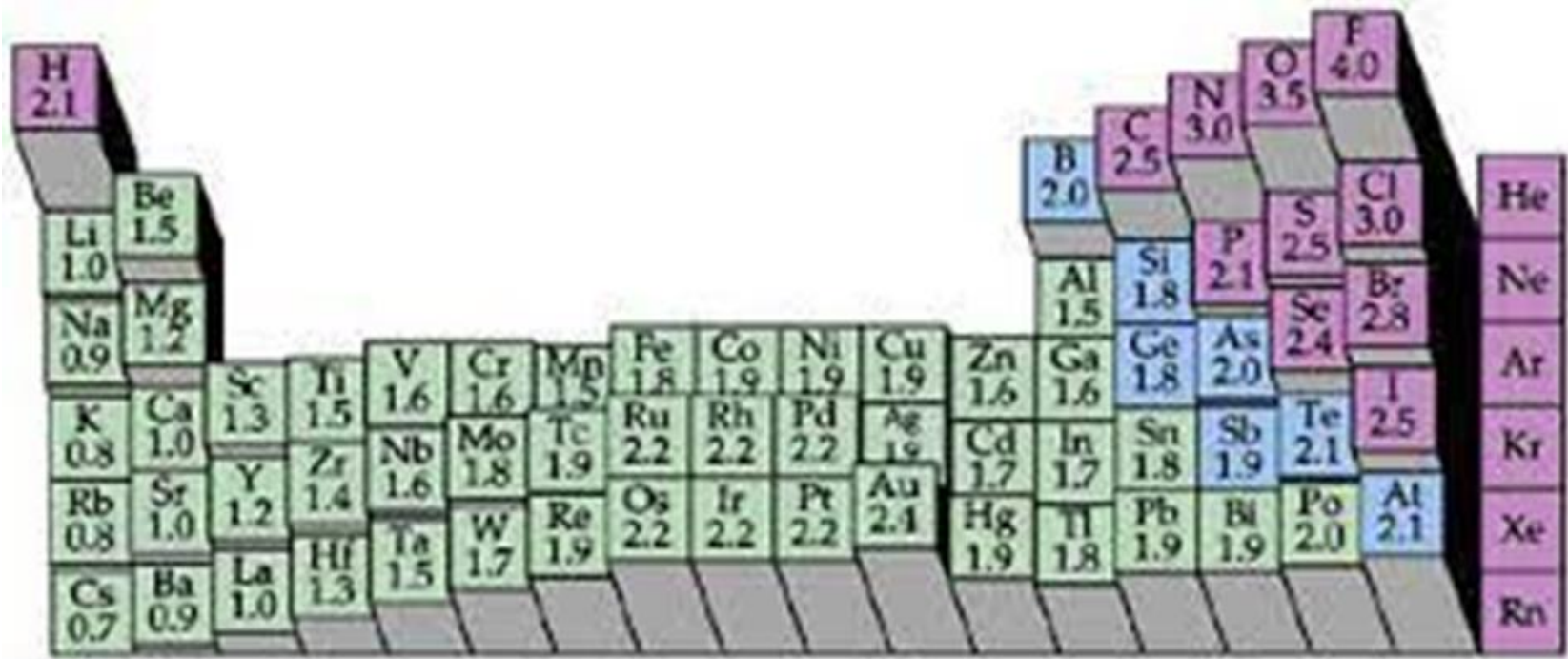
Electronegativity can be understood as a chemical property describing an atom's ability to attract and bind with electrons.

Because electronegativity is a qualitative property, there is no standardized method for calculating electronegativity.

However, the most common scale for quantifying electronegativity is the **Pauling scale**, named after the chemist Linus Pauling.

The numbers assigned by the Pauling scale are dimensionless due to the qualitative nature of electronegativity.

Pauling scale values:

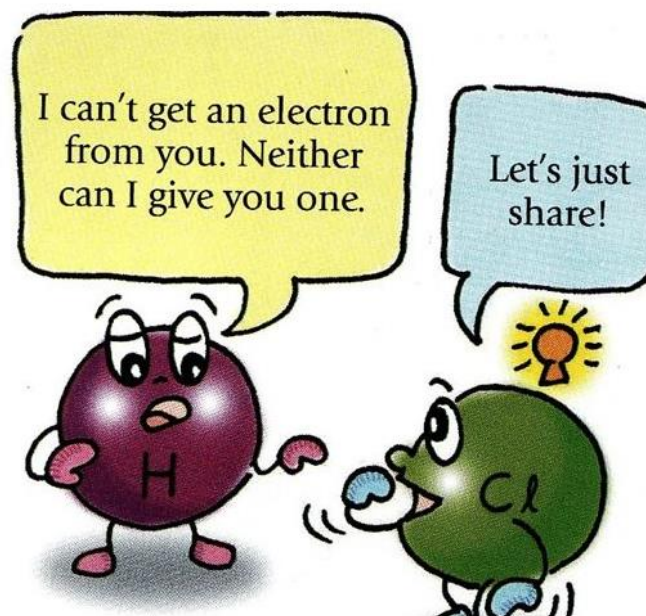




- Chlorine: 3.0
- Bromine: 2.8
- Iodine: 2.5
- Lithium: 1.0
- Sodium: 0.9

## Why do we Need This?

- To determine Bond type of a molecule (non-polar covalent, polar covalent, or ionic)
- To determine whether a reaction will occur and where on a molecule it will occur.





- Sodium Chloride
  - Sodium = 0.9
  - Chloride = 3.0
  - Sodium Chloride:  $3.0 - 0.9 = 2.1$

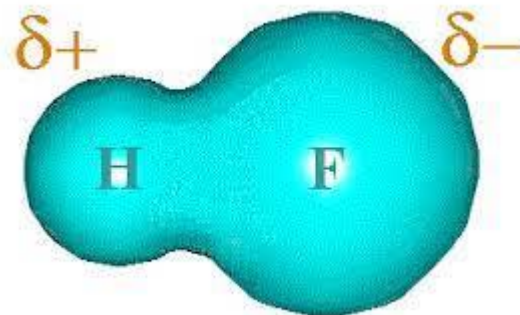
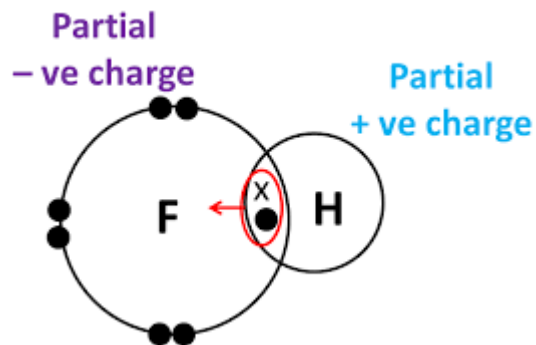
- MgO (Magnesium Oxide)
- Mg = 1.2
- O = 3.5
- $3.5 - 1.2 = 2.3$
- Therefore, another ionic molecule!

- If the number is between 0 and 0.5 the bond is non-polar covalent
- If the number is between 0.5 and 1.8, the bond is polar covalent
- If the number is larger than 1.8, the bond is ionic

- Hydrogen gas ( $H_2$ ):
  - $2.1 - 2.1 = 0$  non-polar covalent
- Hydrogen Bromide (HBr):
  - $2.8 - 2.1 = 0.7$  polar covalent
- Formaldehyde ( $CH_2O$ ):
  - C-H bond:  $2.5 - 2.1 = 0.4$  non-polar covalent
  - C-O bond:  $3.5 - 2.5 = 1.0$  polar covalent
- $SnCl_4$  Tin Chloride
  - $3.0 - 1.8 = 1.2$  polar covalent
- $CBr_4$  Carbon Tetrabromide
  - $2.8 - 2.5 = 0.3$  non-polar covalent

- Hydrogen Fluoride
  - Hydrogen = 2.1
  - Fluoride = 4.0
  - $4.0 - 2.1 = 1.9$
- So it's ionic by the calculations

But it's covalent.



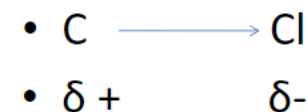
## Where will electrons Spend more Time?

Carbon = 2.5

Or

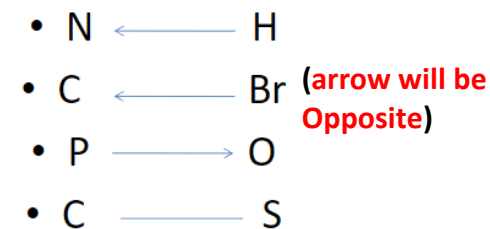
Chlorine = 3.0

Rule: The larger the number, the more electronegative. The more electronegative, the more time electrons spend around that element

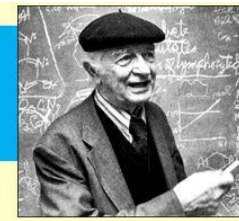


- Arrow ALWAYS goes from + to -

- N-H
  - $3.0 - 2.1 = 0.9$
  - Nitrogen
- C-Br
  - $2.5 - 2.8 = 0.3$
  - Bromine
- P-O
  - $2.1 - 3.5$
  - Oxygen
- C-S
  - $2.5 - 2.5 = 0$
  - Neither!



# Pauling Scale



- Values increase across periods
- Values decrease down groups.
- Fluorine has the highest value.

Electronegativity increases →

Period	Electronegativity increases →																	
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	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 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanides	*	La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27		
Actinides	**	Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3		

The Nobel Prize in Chemistry **1954** was awarded to Linus Carl Pauling "for his research into the nature of the chemical bond and its application to the elucidation of the structure of complex substances."

**1962-** Nobel peace prize

Pauling was one of the founders of the fields of quantum chemistry and molecular biology. Pauling also worked on the structures of biological molecules, and showed the importance of the alpha helix and beta sheet in protein secondary structure. Pauling's approach combined methods and results from X-ray crystallography, molecular model building, and quantum chemistry. His discoveries inspired the work of James Watson, Francis Crick, Maurice Wilkins and Rosalind Franklin on the structure of DNA, which in turn made it possible for geneticists to crack the DNA code of all organisms

## Pauling electronegativity

Pauling first proposed the concept of electronegativity in 1932 to explain why the covalent bond between two different atoms (A–B) is stronger than the average of the A–A and the B–B bonds. According to valence bond theory, of which Pauling was a notable proponent, this "additional stabilization" of the heteronuclear bond is due to the contribution of ionic canonical forms to the bonding.

The difference in electronegativity between atoms A and B is given by:

$$|\chi_A - \chi_B| = (\text{eV})^{-1/2} \sqrt{E_d(\text{AB}) - \frac{E_d(\text{AA}) + E_d(\text{BB})}{2}}$$

where the dissociation energies,  $E_d$ , of the A–B, A–A and B–B bonds are expressed in electronvolts, the factor  $(\text{eV})^{-1/2}$  being included to ensure a dimensionless result. Hence, the difference in Pauling electronegativity between hydrogen and bromine is 0.73 (dissociation energies: H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV)

As only differences in electronegativity are defined, it is necessary to choose an arbitrary reference point in order to construct a scale. Hydrogen was chosen as the reference, as it forms covalent bonds with a large variety of elements: its electronegativity was fixed first. It is also necessary to decide which of the two elements is the more electronegative (equivalent to choosing one of the two possible signs for the square root).

This is usually done using "**chemical intuition**": in the above example, hydrogen bromide dissolves in water to form  $\text{H}^+$  and  $\text{Br}^-$  ions, so it may be assumed that bromine is more electronegative than hydrogen. However, in principle, since the same electronegativities should be obtained for any two bonding compounds, the data are in fact overdetermined, and the signs are unique once a reference point is fixed (usually, for H or F).

# Allred-Rochow electronegativity

Allred-Rochow Electronegativity is a measure that determines the values of the electrostatic force exerted by the effective nuclear charge on the valence electrons. The value of the effective nuclear charges is estimated from Slater's rules. The higher charge, the more likely it will attract electrons. Although, Slater's rule are partly empirical.

To do so, they came up with an equation:

$$\chi_{AR} = ((3590 \times Z_{\text{eff}})/(r_{\text{cov}})^2)) + 0.744$$

At the time, the values for the covalent radius,  $r_{\text{cov}}$ , were inaccurate. Allred and Rochow added certain parameters so that it would more closely correspond to Pauling's electronegativity scale.

H 2.20																
Li 0.97	Be 1.47											B 2.01	C 2.50	N 3.07	O 3.50	F 4.10
Na 1.01	Mg 1.23											Al 1.47	Si 1.74	P 2.06	S 2.44	Cl 2.83
K 0.91	Ca 1.04	Sc 1.20	Ti 1.32	V 1.45	Cr 1.56	Mn 1.60	Fe 1.64	Co 1.70	Ni 1.75	Cu 1.75	Zn 1.66	Ga 1.82	Ge 2.02	As 2.20	Se 2.48	Br 2.74
Rb 0.89	Sr 0.99	Y 1.11	Zr 1.22	Nb 1.23	Mo 1.30	Te 1.36	Ru 1.42	Rh 1.45	Pd 1.35	Ag 1.42	Cd 1.46	In 1.49	Sn 1.72	Sb 1.82	Te 2.01	I 2.21
Cs 0.86	Ba 0.97	La 1.08	Hf 1.23	Ta 1.33	W 1.40	Re 1.46	Os 1.52	Ir 1.55	Pt 1.44	Au 1.42	Hg 1.44	Tl 1.44	Pb 1.55	Bi 1.67	Po 1.76	At 1.90

In this table, the electronegativities increases from left to right just like Pauling's scale because the  $Z$  is increasing. As we go down the group, it decreases because of the larger atomic size that increases the distance between the electrons and nucleus.

## Mulliken's electronegativity

A method for estimating electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966) who noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions.

Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions.

Mulliken recognized that an atom's tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity.

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (  $E_{I1}$  ) and the electron affinity (  $E_{ea}$  ) should be a measure of the tendency of an atom to attract electrons. As this definition is not dependent on an arbitrary relative scale, it has also been termed **absolute electronegativity**. Using our definition of electron affinity, we can write Mulliken's original expression for electronegativity as follows: Mulliken's definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in Equation 1 to make sure that we are adding two positive numbers in the numerator.

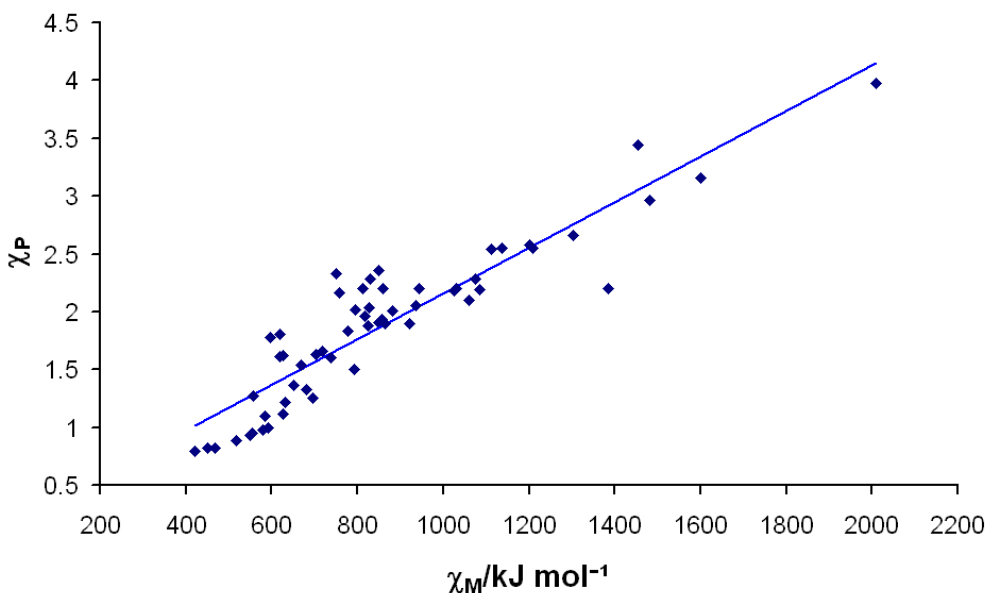
$$\chi = (E_{I1} + |E_{ea}|) / 2 \quad \dots (1)$$

Elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation 1, so their electronegativity is high. Elements with a small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation 1, so they have a low electronegativity. Inserting the appropriate data into Equation 1 gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol.

To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by **252.4 kJ/mol**, which gives Pauling's value

However, it is more usual to use a linear transformation to transform these absolute values into values that resemble the more familiar Pauling values. For ionization energies and electron affinities in electron volts (eV):

$$\chi_{Mulliken} = 0.187(E_{I_1} + E_{ea}) + 0.17$$



The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006. The Mulliken electronegativity of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the Mulliken chemical potential is a finite difference approximation of the electronic energy with respect to the number of electrons., i.e.,

$$\mu_{Mulliken} = -\chi_{Mulliken} = -(E_{I_1} + E_{ea})/2$$

All electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on **the properties of individual atoms** and the Pauling scale is based on **the properties of atoms in molecules**, they both apparently measure the same basic property of an element.

Good correlation exist between Mullikin and Pauling electronegativities for the atoms

**Although Pauling electronegativities are usually what are found in textbooks, the Mulliken electronegativity more intuitively corresponds to the "ability of an atom to draw electrons toward itself in bonding," and is probably a better indicator of that property. However, because of the good correlation between the two scales, using the Pauling scale is sufficient for most purposes.**

Electronegativity mainly depends upon oxidation state of the atom and nature of hybrid orbitals which are used for bonding. For any particular atom, as oxidation state increases the electronegativity value also increases.

Among the different atomic orbitals, tendency to penetrate varies as-  $s > p > d > f$ . Hence hybrid orbital which has higher contribution from s-orbital will experience higher  $Z_{\text{eff}}$  and hence show higher electronegativity. Thus electronegativity increases as  $sp^3 < sp^2 < sp$ , among hybrid orbitals with gradual increase in s-character from 25% to 50%.

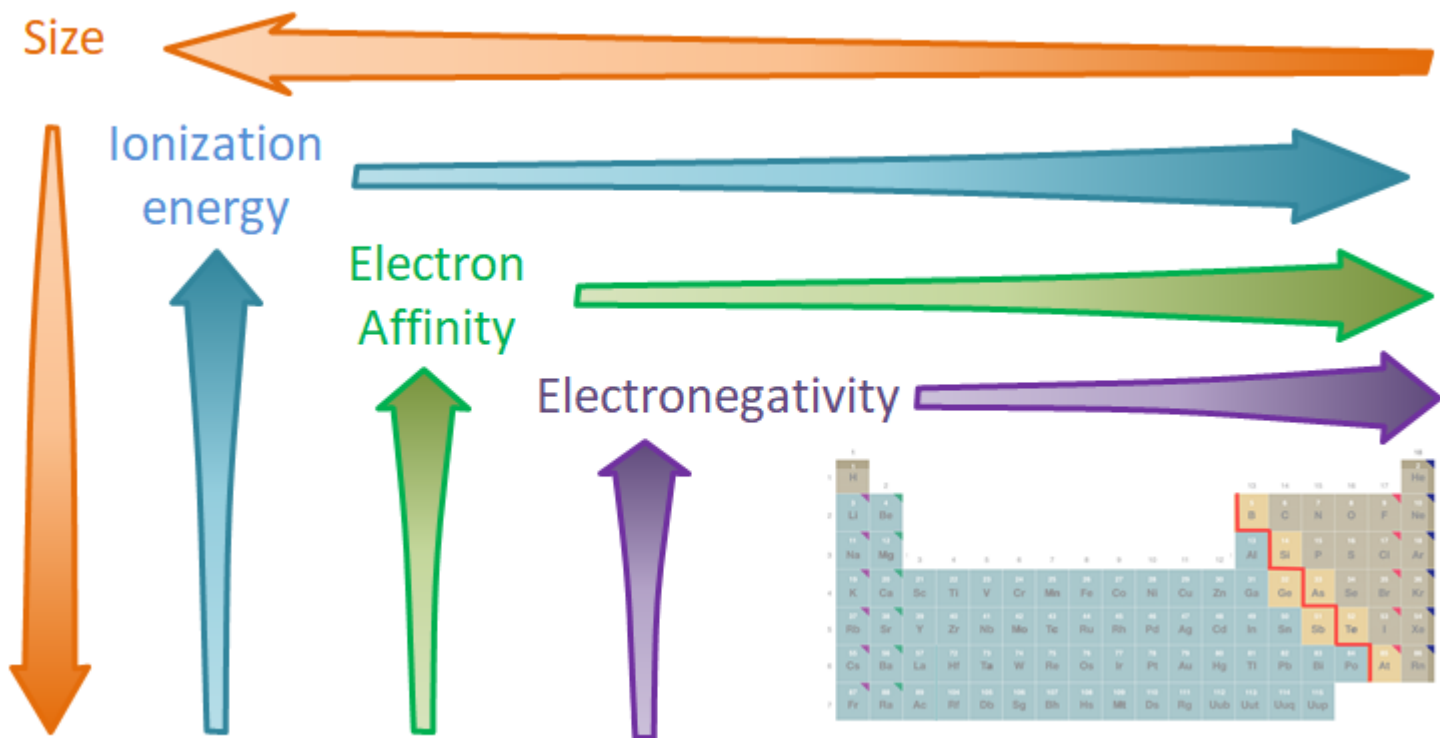
Thus for hybridized orbitals, acidity increases and basicity increases with increase in s-character of hybrid orbital.

**For example,**

Acidity:  $\text{CH}_4$  ( $sp^3$ )  $<$   $\text{C}_2\text{H}_4$  ( $sp^2$ )  $<$   $\text{C}_2\text{H}_2$  ( $sp$ )

Basicity:  $(\text{CH}_3)_3\text{N}$  ( $sp^3$ )  $>$   $\text{C}_5\text{H}_5\text{N}$  ( $sp^2$ )  $>$   $\text{CH}_3\text{CN}$  ( $sp$ )





Atomic size increases down a group as the valence orbital becomes larger ( $n$  increases) and roughly decreases across a row as the effective nuclear charge increases.

Ionization energy decreases down a group as the valence orbital becomes larger and roughly increases across a row as the effective nuclear charge increases.

Electron affinity decreases down a group as the valence atomic orbital becomes larger and roughly increases across a row as the effective nuclear charge increases.

Electronegativity decreases down a group as the lowest incompletely occupied atomic orbital becomes larger and roughly increases across a row as the effective nuclear charge increases.

**Metal-Nonmetal Line**

**Metals**  
(below and to the left of the line)

**Nonmetals**  
(above and to the right of the line)

**Metalloids**  
(on the line)

1	2																18
1 H																	2 He
3 Li	4 Be																10 Ne
11 Na	12 Mg																18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup			
Lanthanides			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

The metals towards lower left of the periodic table form metallic solids held together by delocalized bonding. As a result metals are –

- malleable (able to be hammered into sheets) and ductile (able to be pulled into wires), since metals' solid state lattices may be deformed by dislocation movement (slip) without significantly disrupting the bonding.
- exhibit a high thermal conductivity and high electrical conductivity. Since they have an incompletely filled valence band delocalized throughout the structure it is easy to transmit heat and charge by moving their electrons around.

In contrast the **nonmentals** towards the upper right of the periodic table form molecular compounds and network covalent solids. In general these elements tend to exist as

- be liquids, gases, or brittle solids. When present as solids nonmetals tend to be brittle since deformation involves rupturing covalent bonds in the case of covalent solids or the rupture of intermolecular forces in the case of molecular solids.

- have low thermal and electrical conductivity. Since for molecular solids the transfer of energy or electrons via collisions or through space is much much slower and, for network covalent solids held together by strong sigma bonds involves excitation of electrons across a reasonably large band gap. Note that this is only a tendency. Network covalent solids held together by weaker covalent bonds or  $\pi$ -bonds sometimes have small or nonexistent band gaps. For example, the graphite allotrope of carbon is an outstanding electrical conductor because its  $\pi$ -valence band and  $\pi^*$ -conduction band overlap, leaving no band gap.

**The metalloids** along the metal-nonmetal line form solids that exhibit bonding patterns and properties intermediate between those of metals and nonmetals. This is because in reality there is a graduation in element properties as one moves from the lower left to the upper right of the periodic table. Consequently, although the distinction between metals, nonmetals, and metalloids can be a helpful one these categories and **should not be understood too rigidly**.

The same is true of the tendency of metals and nonmetals to form ionic compounds with one another, owing to the tendency of metals to lose electrons and nonmentals to gain them. In practice, there is a graduation in ionic character based on the difference in the elements' electronegativities and the size/polarizability of the atoms involved. As a result many compounds between metals and nonmetals may be profitably thought of as involving polar covalent bonds.

## Why Hg is liquid?

Mercury-mercury bonding is very weak because its valence electrons are not shared easily. Mercury is the only metal that doesn't form diatomic molecules in the gas phase.

Heat easily overcomes the weak binding between mercury atoms, mercury boils and melts at a lower temperature than any other metal.

The electrons are moving so fast and close to the nucleus that they exhibit relativistic effects, behaving as if they were more massive than slower-moving electrons.

- 1) Filled orbital
- 2) Relativistic effect

${}^2\text{He}_{(\text{gas})}$ $1s^2$
${}^{10}\text{Ne}_{(\text{gas})}$ $[\text{He}] 2s^2, 2p^6$
${}^{18}\text{Ar}_{(\text{gas})}$ $[\text{Ne}] 3s^2, 3p^6$
${}^{36}\text{Kr}_{(\text{gas})}$ $[\text{Ar}] 3d^{10}, 4s^2, 4p^6$

Filled orbital is not the only criterion.

Gr. 8A elements having complete valence shell exist in gaseous form.

But noble gases belong to p block of periodic table, having chemistry entirely different from mercury of d block.

**Mercury is the only elements of d block that is liquid at room temperature.**

${}^{30}\text{Zn}$ $[\text{Ar}] 3d^{10} 4s^2$
${}^{48}\text{Cd}$ $[\text{Kr}] 4d^{10} 5s^2$
${}^{80}\text{Hg}$ $[\text{Xe}] 4f^{14} 5d^{10} 6s^2$

## Liquid state and theory of relativity

Due to special relativity the apparent mass of an object increases as its velocity approaches the speed of light.

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

$m$  rest/ invariant mass of body

$m_0$  relativistic mass

$v$  velocity of body

$c$  speed of light

$$v = \frac{Z\alpha c}{n} \approx \frac{Zc}{137n}$$

Equation 1

Where  $c$  is the speed of light and

$$\alpha = \frac{e^2}{2\epsilon_0 hc} = \frac{1}{137.035999...}$$

$\alpha$  is the fine structure constant ( $e$  is the elementary charge,  $h$  is Planck's constant, and  $\epsilon_0$  is the permittivity of free space).

Bohr's theory  $v \propto z$  (atomic number)

The electrostatic potential between nucleus and electron decreases with increasing distance.

PE decrease; PE+KE = constant, so KE needs to increase

So  $v$  (velocity of electron needs to increase)



### Relativistic effect for lighter elements



The velocity is insignificant For light elements compared to the speed of light so relativity is not considered.

### Relativistic effect for heavier elements



For the 1s electron of mercury relativistic effect becomes significant

The electron approaches about 58% of the speed of light

Decrease in orbital radius cause stronger attraction  
Between nucleus and electrons

d and f orbitals are more diffuse so they insufficiently shield the s –electrons, contributing towards orbital decrease

Due to relativistic shrinkage also, it is too difficult for Hg to share its valence electrons to the nearby atoms to form Metallic bond.

### Mass increase results in a 23% decrease in the orbital radius

$$mvr = \frac{nh}{2\pi}$$

$$vr = \frac{nh}{2\pi m}$$

$$\text{mass} \propto \frac{1}{\text{orbital radius}}$$

Because the radius of an electron orbital is inversely proportional to the mass of atom

1. Chlorine, bromine and iodine form a Dobereiner's triad. The atomic masses of chlorine and bromine are 35.5 and 81.2 respectively. Predict the atomic mass of iodine.
2. Atoms of seven elements A, B, C, D, E, F and G have a different number of electronic shells but have the same number of electrons in their outermost shells. The elements A and C combine with chlorine to form an acid and common salt respectively. The oxide of element A is liquid at room temperature and is a neutral substance, while the oxides of the remaining six elements are basic in nature. Based on the above information, answer the following questions:
  - What could the element A be?
  - Will elements A to G belong to the same period or same group of the periodic table?
  - Write the formula of the compound formed by the reaction of the element A with oxygen,
  - Show the formation of the compound by a combination of element C with chlorine with the help of electronic structure.
  - What would be the ratio of number of combining atoms in a compound formed by the combination of element A with carbon?
  - Which one of the given elements is likely to have the smallest atomic radius?

3. Atoms of eight elements A, B, C, D, E, F, G and H have the same number of electronic shells but different number of electrons in their outermost shells. It was found that elements A and G combine to form an ionic compound which can also be extracted from sea water. Oxides of the elements A and B are basic in nature while those of E and F are acidic. The oxide of element D is almost neutral. Answer the following questions based on the information given herein:

To which group or period of the periodic table do the listed elements belong?

Which one of the eight elements is likely to be a noble gas?

Which one of the eight elements would have the largest atomic radius?

Which two elements amongst these are likely to be non-metals?

Which one of these eight elements is likely to be a semi-metal or metalloid?

4. Two elements X and Y belong to group 1 and 2 respectively in the same period of periodic table. Compare them with respect to:

periodic table from the left to the right and why?

the number of valence electrons in their atoms

their valencies

metallic character

the sizes of their atom

formulae of their oxides

formulae of their chlorides



What is the correct order of electronegativity among the following options?

- a)  $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$
- b)  $\text{Li} < \text{K} < \text{Na} < \text{Rb} < \text{Cs}$
- c)  $\text{Li} > \text{Na} > \text{K} > \text{Cs} > \text{Rb}$
- d)  $\text{Li} > \text{Na} > \text{K} = \text{Rb} > \text{Cs}$

There are only two elements that are liquid at room temperature, mercury is one, can you name the other?

Which element's existence was first predicted by Mendeleev in 1871, who named it "eka-aluminium" because he knew it would go below aluminum on the periodic table?