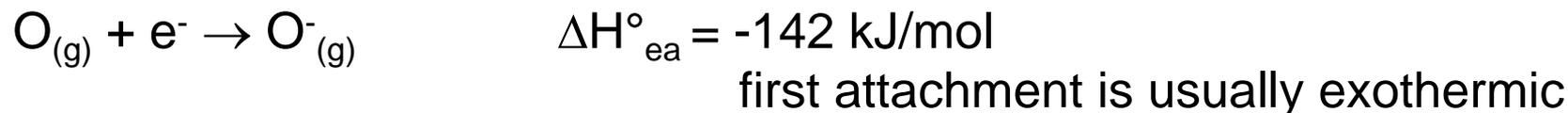


Electron Attachment Enthalpy, ΔH°_{ea}

The enthalpy change for the gain of an electron, $E_{(g)} + e^- \rightarrow E^-_{(g)}$

$$\text{Electron Affinity: } EA = -\Delta H^\circ_{ea} + 5/2 RT$$

$$EA = -\Delta H^\circ_{ea}$$



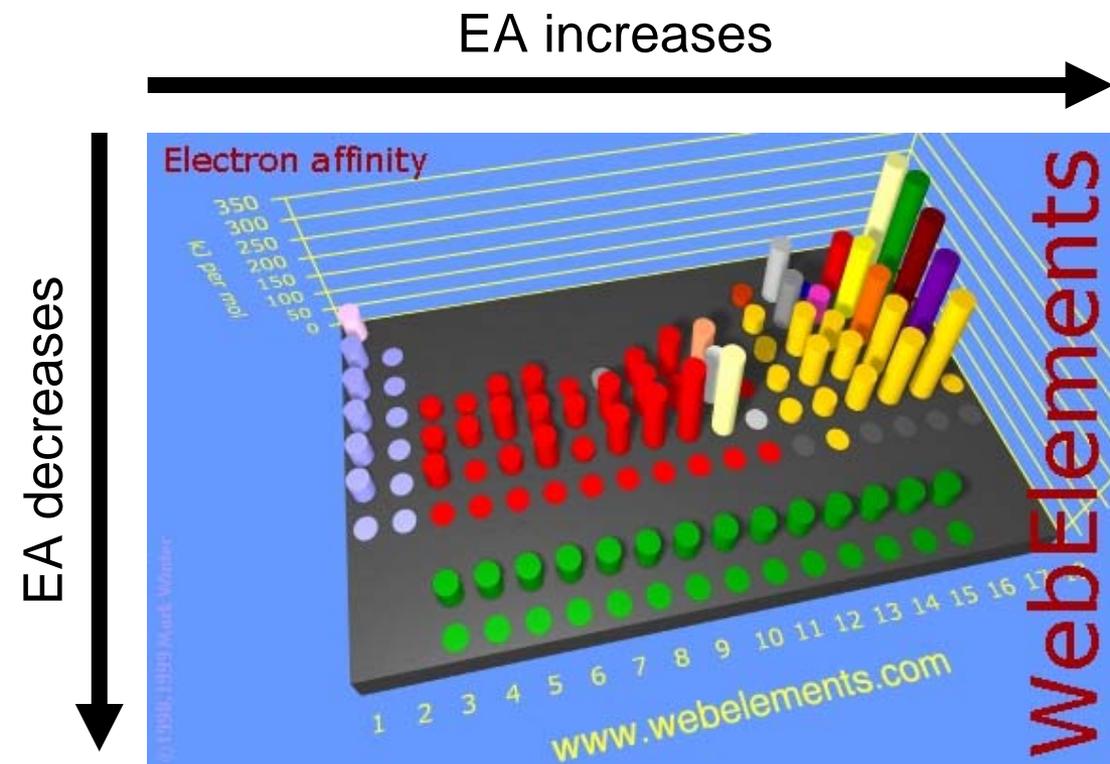
Other factors favour the presence of O^{2-} when it is found in molecules and ionic solids.

Overall trends are not as apparent, however:

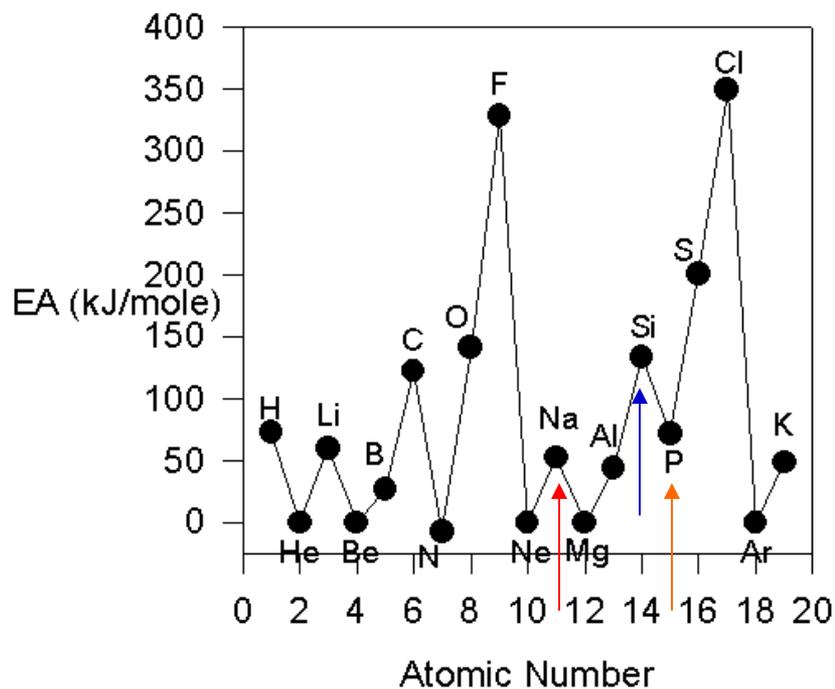
Highest values EA for halogens (Group 17) because they have very high Z^* and the additional electron completes the shell.

Negative values of EA for alkaline earth metals (Group 2) because the additional electron goes into the less-stable p subshell (smaller Z^*).

Negative values of EA for noble gases (Group 18) because extra electron has to go into next shell ($n+1$)s.



Electron Affinity versus Atomic Number



→ Na: $[\text{Ne}]3s^1$ – additional electron makes $[\text{Ne}]3s^2$ which is a full subshell.

→ Si: $[\text{Ne}]3s^2 3p^2$ – additional electron makes $[\text{Ne}]3s^2 3p^3$ which is a more stable half-filled subshell so EA is high.

→ P: $[\text{Ne}]3s^2 3p^3$ – additional electron makes $[\text{Ne}]3s^2 3p^4$ which requires electron pairing so EA is low.

The gain and loss of electrons drives some of the most powerful forms of chemical reactions.

Reduction – gain of electrons

Oxidation – loss of electrons

ΔE° , the *standard potential* for an equilibrium, gives access to ΔG° through the following relationship:

$$\Delta G^\circ = - n\mathcal{F} \Delta E^\circ$$

where,

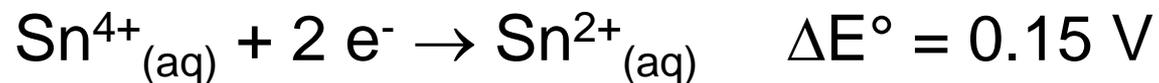
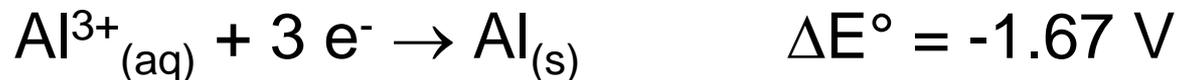
n = number of electrons involved

\mathcal{F} = Faraday's constant = $96.4867 \text{ kJ mol}^{-1} \text{ V}^{-1} (\text{e}^-)^{-1}$

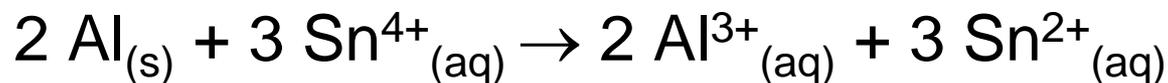
Note: if $\Delta G^\circ < 0$, then must be $\Delta E^\circ > 0$

So favourable reactions must have $\Delta E^\circ > 0$

Half-Cell Reduction Potentials



thus for:



$$\Delta E^{\circ} = -(-1.67 \text{ V}) + (0.15 \text{ V}) = 1.82 \text{ V} \text{ for 6 electrons}$$

$$\text{So: } \Delta G^{\circ} = -nF \Delta E^{\circ} = -(6 \text{ e}^{-})F(1.82 \text{ V}) = -1054 \text{ kJ/mol}$$

Chem 59-250 Balancing RedOx Reactions

1. Identify the formal oxidation of each element (and identify which element(s) are getting oxidized and which are getting reduced).
2. Write an appropriate half-cell for each element undergoing oxidation or reduction.
3. Balance the electrons involved for both oxidation and reduction (i.e. the number of electrons must be conserved)
4. Balance the charges on each side of the reaction by adding (H^+ for acidic conditions, OH^- for basic conditions).
5. Balance the remaining O atoms and H atoms by adding water (H_2O) to the appropriate side of the equation.

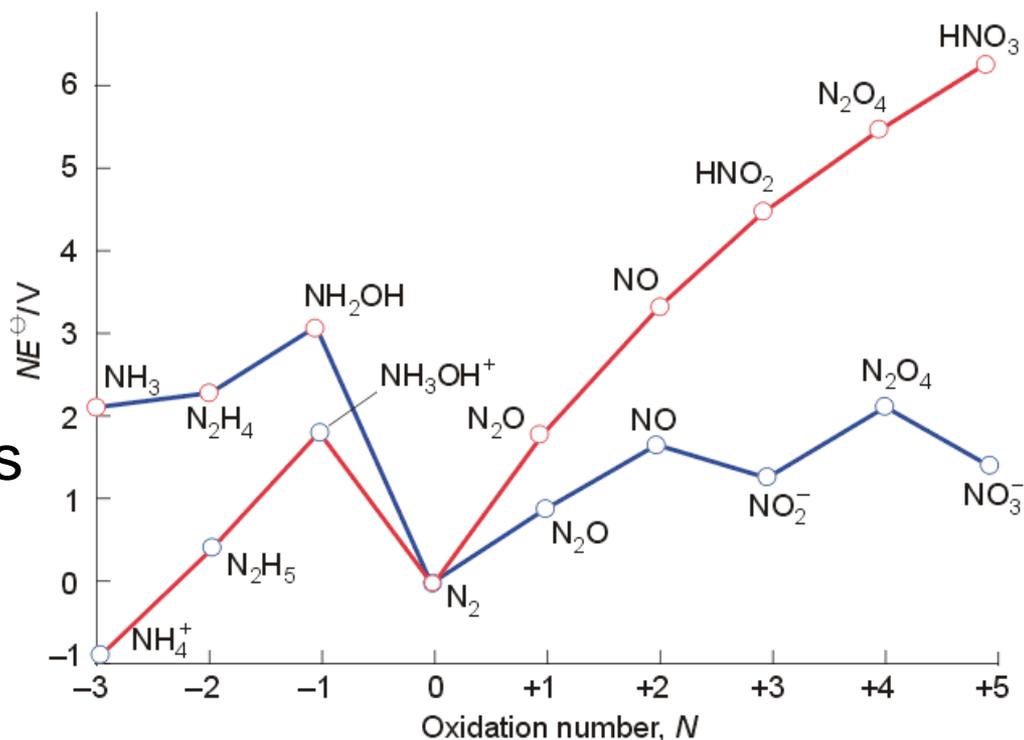
Oxidation state diagrams (Frost Diagrams)

Relative Energy vs. Oxidation State (under certain conditions)

Provides:

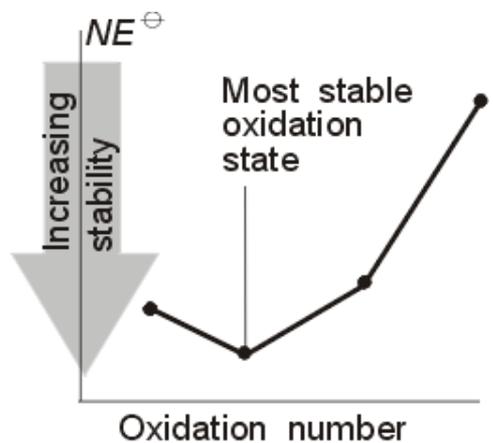
- Relative stability of oxidation states

- Energies available or required for RedOx reactions (the slope between reactant and product)

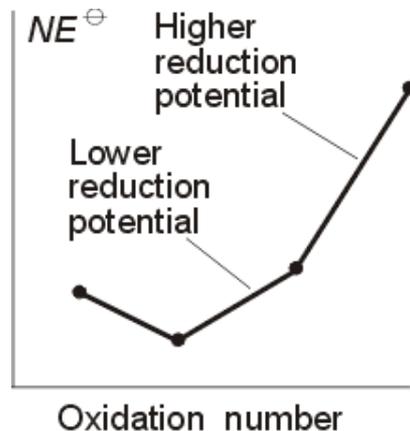


Oxidation state diagrams (Frost Diagrams)

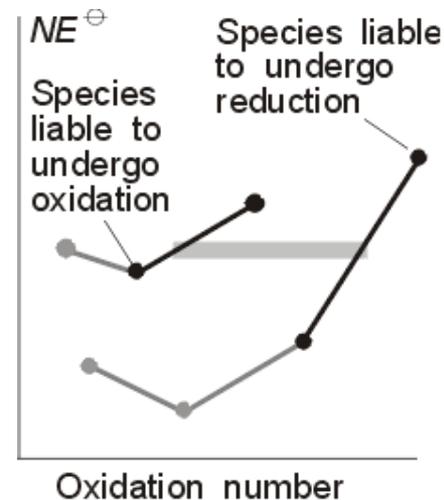
Some important information provided by Frost diagrams:



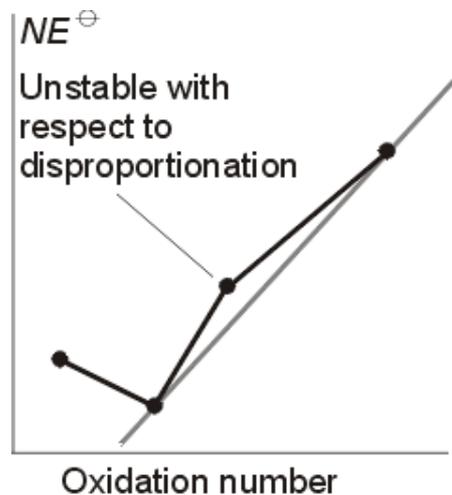
1



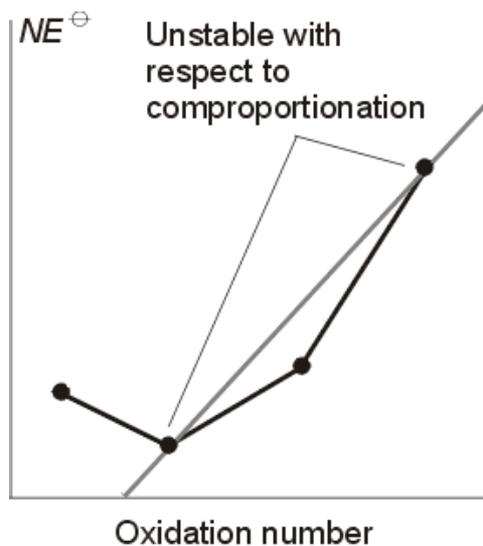
2



3

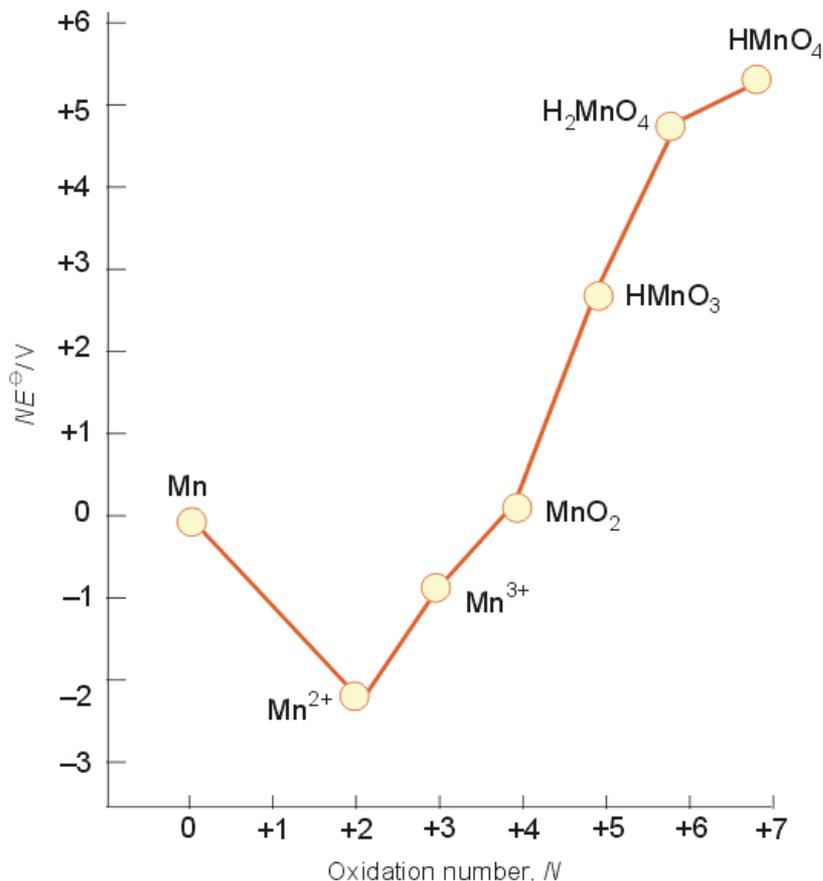


4



6

The diagram for Mn displays many of these features.



The most useful aspect of Frost diagrams is that they allow us to predict whether a RedOx reaction will occur for a given pair of reagents and what the outcome of the reaction will be. This is described in the handout.

Electronegativity, χ

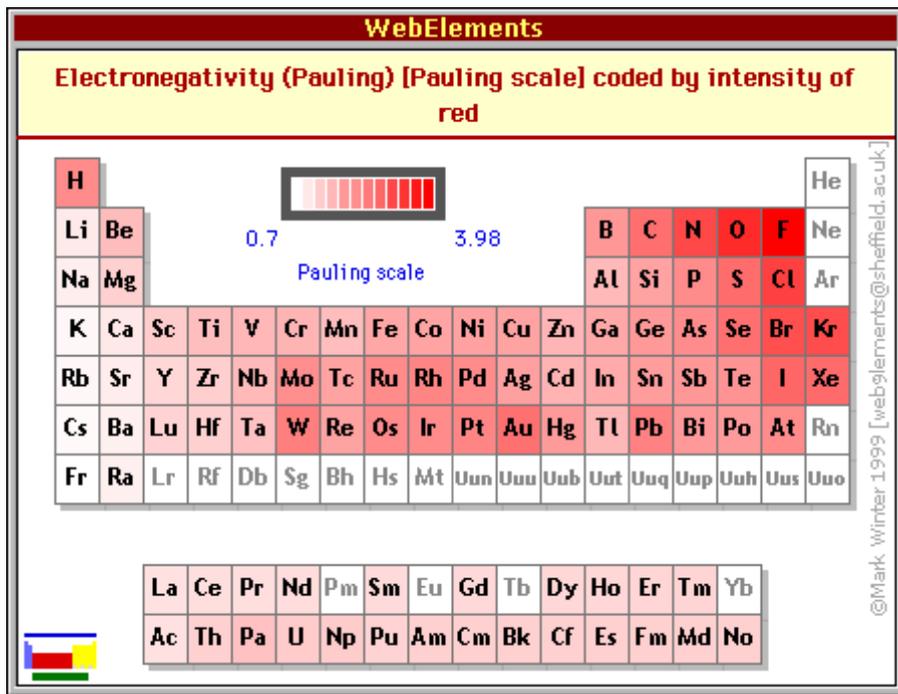
The ability of an atom *in a molecule* to attract electrons in a bond to itself.

χ increases 



Linus Pauling

χ decreases 

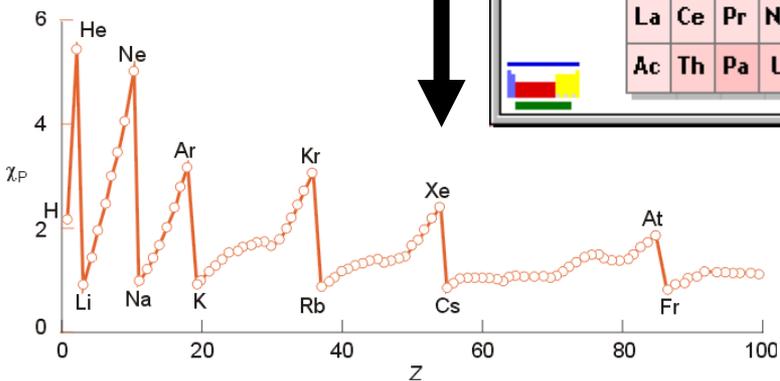


First Year rule

$\Delta\chi > 2$: ionic

$2 > \Delta\chi > 0.5$: polar

$\Delta\chi < 0.5$: covalent



Traditional scale goes from 0 to 4 with χ of F set to 4.

Pauling's definition:

Pauling reasoned that the dissociation energy of a purely covalent bond A-B should be the mean of the dissociation energies for the homonuclear bonds A-A and B-B. Any additional energy must be caused by electrostatic attraction between A and B (attributed to ionic character in a bond). The ionic character must be related to the difference in the *electronegativities* of A and B. He calculated this difference as follows:

$$D_{(A-B),\text{theory}} = \frac{1}{2} (D_{(A-A)} + D_{(B-B)})$$

$$\Delta'_{(A-B)} = D_{(A-B),\text{experimental}} - D_{(A-B),\text{theory}}$$

$$\chi_A - \chi_B = 0.102 (\Delta'_{(A-B)})^{1/2}$$

$\Delta'_{(A-B)}$ is the *ionic resonance energy* in kJ/mol ($\Delta_{(A-B)}$ is in eV)

A-B \leftrightarrow A⁺ B⁻
0.102 is a conversion from kJ/mol to eV

Chem 59-250 An example calculation for H-F

$$D_{(\text{H-F}),\text{theory}} = \frac{1}{2} (D_{(\text{H-H})} + D_{(\text{F-F})}) = \frac{1}{2} (436 + 158) = 297 \text{ kJ/mol}$$

$$\Delta'_{(\text{H-F})} = D_{(\text{H-F}),\text{experimental}} - D_{(\text{H-F}),\text{theory}} = 566 - 297 = 269 \text{ kJ/mol}$$

$$\chi_{\text{F}} - \chi_{\text{H}} = 0.102 (\Delta'_{(\text{H-F})})^{1/2} = 0.102 (269)^{1/2} = 1.67$$

Pauling set $\chi_{\text{F}} = 4.0$ so: $\chi_{\text{H}} = 4.0 - 1.67 = 2.32$

Note: 2.32 is different than the value of 2.2 you see in tables because Pauling used the geometric mean instead of the arithmetic mean.

Similar calculations were used to determine χ for the other elements.

$$(\Delta_{(\text{H-Cl})})^{1/2} = 0.98 \text{ eV relative to H so } \chi_{\text{Cl}} \approx 3.2$$

$$(\Delta_{(\text{H-Br})})^{1/2} = 0.73 \text{ eV relative to H so } \chi_{\text{Br}} \approx 2.9$$

$$(\Delta_{(\text{H-I})})^{1/2} = 0.25 \text{ eV relative to H so } \chi_{\text{I}} \approx 2.5$$

Mulliken's definition:

Mulliken figured that the electronegativity of an element must be related to the energies of gaining and losing electrons. Specifically an atom that binds its electrons strongly (large ΔH_{ie}°) and gains other electrons readily (very positive EA or very negative ΔH_{ea}°) should do the same in molecules. Thus Mulliken calculated the electronegativity of an atom as the mean of the ionization potential and the electron affinity.



Robert
Mulliken

For A-B, the electronegativity difference between A^+B^- and A^-B^+ is given by:

$$\chi_A - \chi_B = \frac{1}{2} ([IP_A + EA_A] - [IP_B + EA_B])$$

$$\chi_A = \frac{1}{2} ([IP_A + EA_A]) \quad (\text{these are then scaled to fit the } \approx 0\text{-}4 \text{ scale})$$

This method makes a lot of sense, but is not used because values of ΔH_{ea}° have not been accurately determined for many elements.

The Allred-Rochow definition:

The assumption is that the force that will draw an electron toward an atom is proportional to the effective nuclear charge of that atom and related to the distance of the electron from the nucleus.

$$\text{Force} = \frac{Z^* e^2}{4\pi\epsilon_0 r^2}$$

Z^* = effective nuclear charge

e = charge of electron

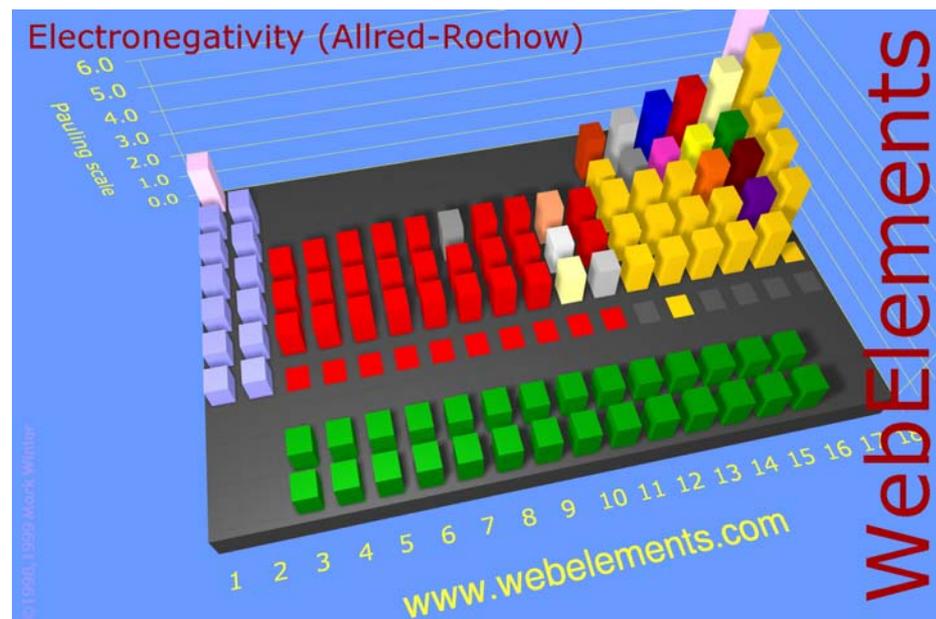
ϵ_0 = permittivity of a vacuum

r = atomic radius

The equation:

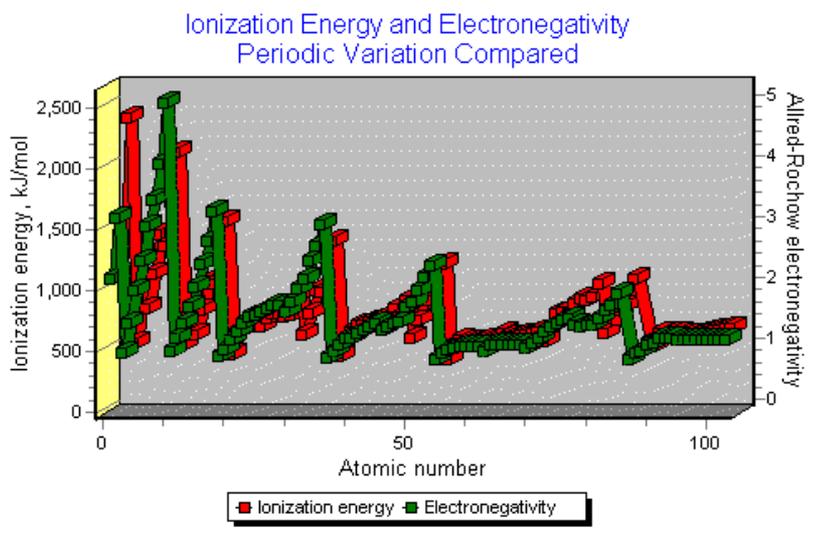
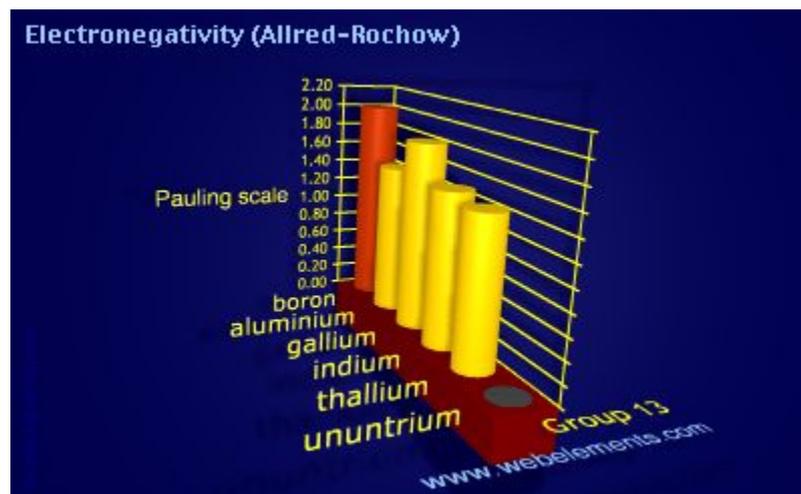
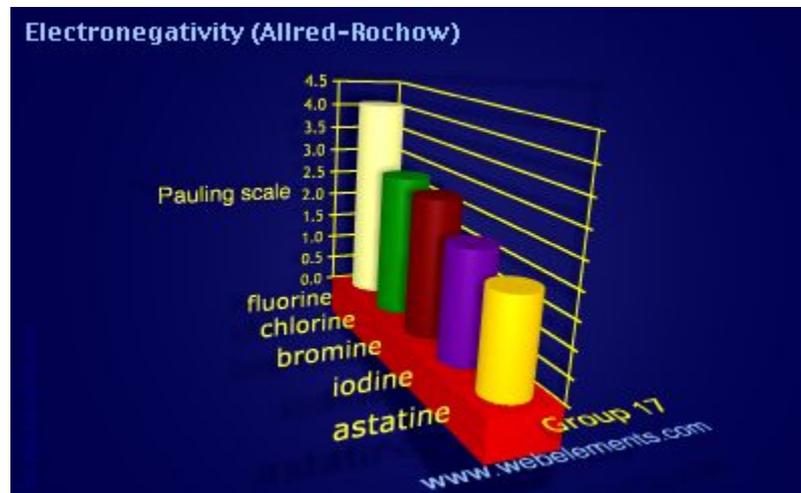
$$\chi = 0.359 (Z^*/r^2) + 0.744$$

puts the calculated values on the Pauling scale. This definition is useful because it can be applied to many more atoms and is one of the most used scales.



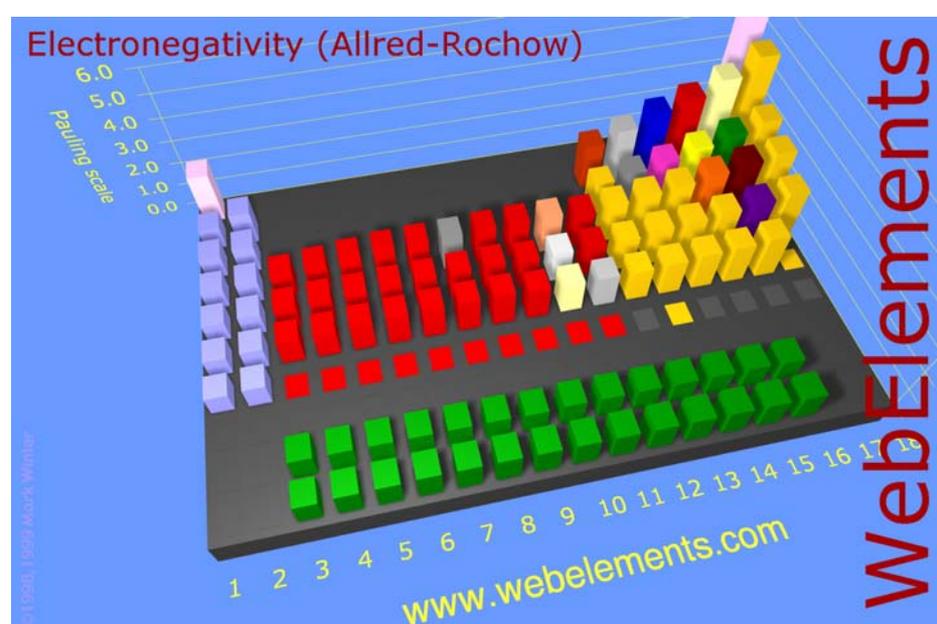
There are several other definitions based on different assumptions and methods, such as quantum mechanical calculations (Boyd) or spectroscopic measurements (Allen), but the values for elements usually end up around the same.

Trends in electronegativities are similar to those found for ionization enthalpies.

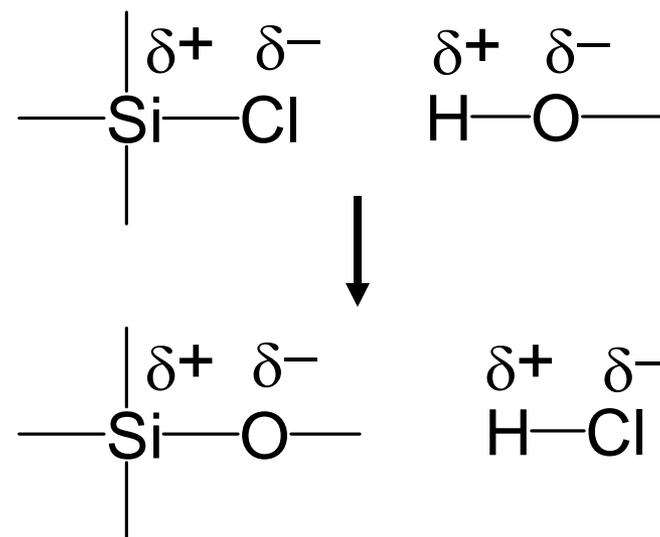


The trends in electronegativities and ionization enthalpies explain many features of chemistry such as the “diagonal relationship” (\mathcal{X}) and the position of the metallic and non-metallic elements (ΔH°_{ie}).

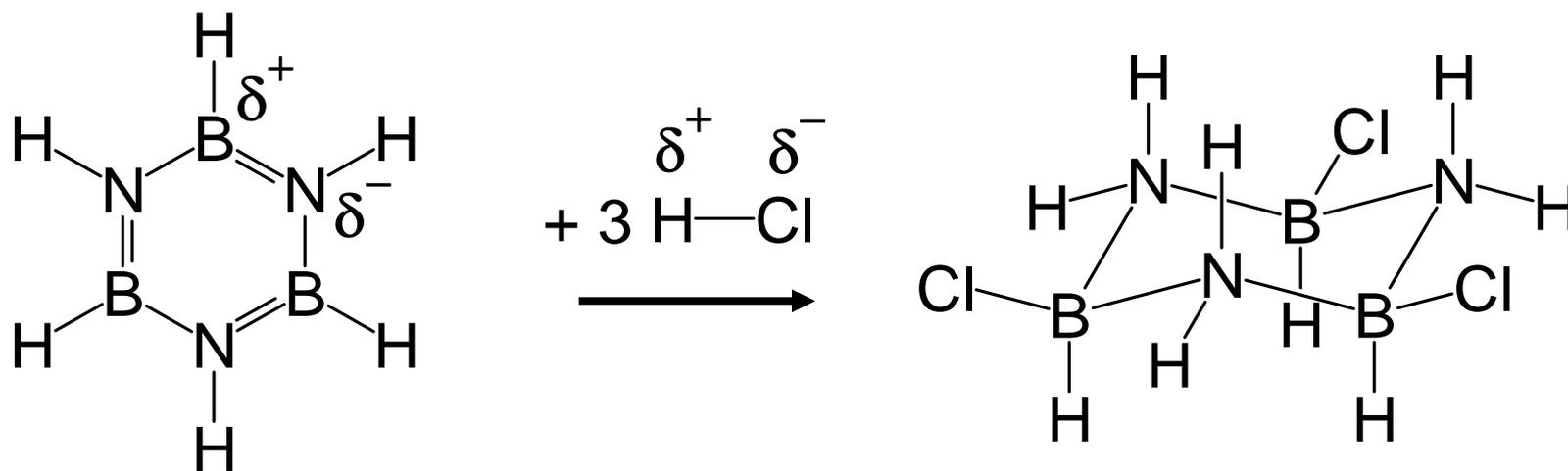
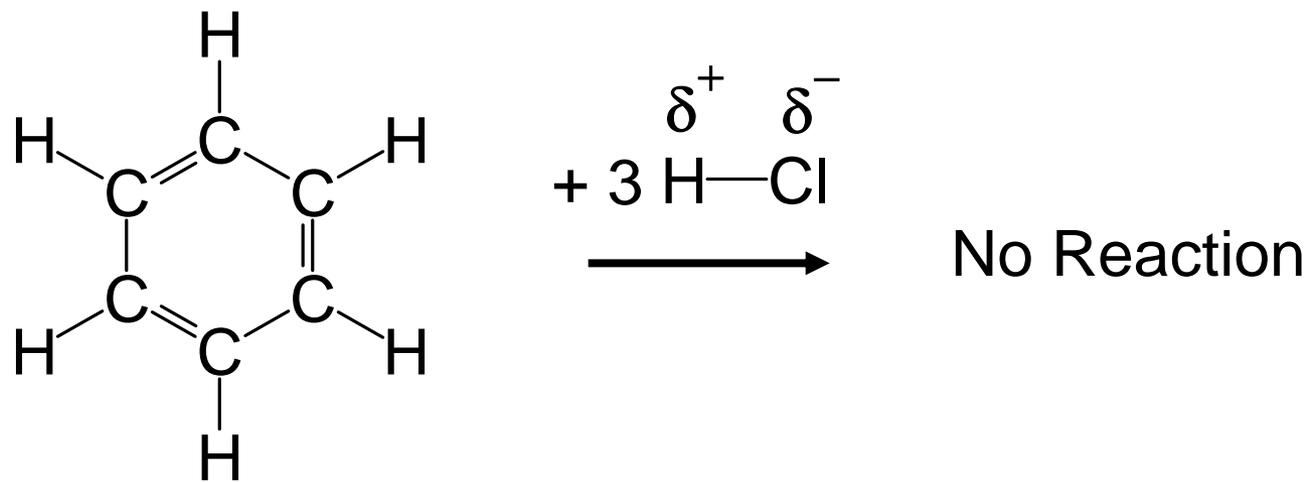
Electronegativity also lets us predict the polarity of bonds and chemical reactivity.



IA												IIIA		IVA	VA	VIA	VIIA	VIIIA	
1 H 1.01												5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18		
3 Li 6.94	4 Be 9.01											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95		
11 Na 22.99	12 Mg 24.30	III B	IV B	V B	VI B	VII B	VIII B	VIII B	VIII B	I B	II B	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95		
19 K 39.1	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3		
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 181.0	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra 226.0	89 Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)											
* Lanthanide Series			58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0			
** Actinide Series			90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)			



Electronegativity lets us predict the polarity of bonds and explains differences in chemical reactivity.



We will examine the effects that electronegativity differences have on the bonding in compounds in much more detail later.

Electronegativity also lets us predict the acidity of some binary element hydrogen compounds. Remember that $\chi(\text{H}) = 2.2$

χ increases, acidity increases



Going from left to right in a period χ increases.

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES				
1 H 1.00797														1 H 1.00797	2 He 4.0026				
3 Li 6.939	4 Be 9.0122													5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183
11 Na 22.9898	12 Mg 24.312													13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30		
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (264)	108 Hs (265)	109 Mt (266)	110 ? (267)	111 ? (268)	112 ? (269)								

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.907	144.24	(147)	150.35	151.96	157.25	158.924	162.50	164.930	167.26	168.934	173.04	174.97

† Actinide Series

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	(231)	238.03	(237)	(242)	(243)	(247)	(247)	(249)	(254)	(253)	(256)	(256)	(257)

E.g. Going from Li to F:
 $\chi(\text{Li}) = 0.9$ so the polarization for an Li-H bond is: $\text{Li}^{\delta+}-\text{H}^{\delta-}$ (“hydridic”)

$\chi(\text{C}) = 2.5$ so the C-H bond is not polarized and not basic or acidic

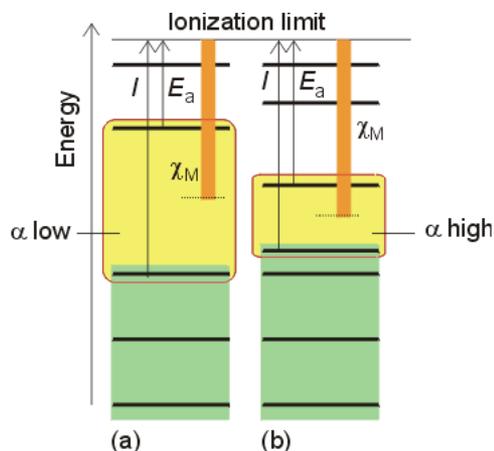
$\chi(\text{F}) = 4.0$ so the polarization for an F-H bond is: $\text{F}^{\delta-}-\text{H}^{\delta+}$ (“protic”)

A similar approach can be used to predict the acidity/basicity of E-O-H bonds.

Please note that going down a group, the element-H bonds get weaker (e.g.: $E_{\text{O-H}} > E_{\text{S-H}} > E_{\text{Se-H}}$) thus the acidity of the compounds increases.

Polarizability and Hard and Soft Atoms

The polarizability, α , of an atom is its ability to be distorted by the presence of an electric field (such as a neighbouring ion). The more easily the electron cloud is distorted, the higher α . This happens primarily with large atoms and anions that have closely spaced frontier orbitals (HOAO and LUAO).



α decreases

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VVA	VIA	VIIA	INERT GASES		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H	He																
3	4											9	10				
Li	Be											B	C	N	O	F	Ne
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	?	?	?	?	?	?	?	?	?
(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)	(123)
<small> Numbers in parenthesis are exact numbers of most stable or most common isotopes. Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights. The group designations used here are the former IUPAC nomenclature. </small>																	

α increases

The hardness, η , of an atom is a related quantity. Hard atoms (high η) bind their electrons tightly and are not easily polarized. Soft atoms (low η) bind their electrons loosely and have a higher α .

$$\eta = \frac{1}{2} ([IP_A - EA_A]) \text{ in eV}$$

$$\eta_{Si} \approx 3.4$$

$$\eta_F \approx 7.0$$

$$\eta_{Sn} \approx 3.0$$

$$\eta_I \approx 3.7$$

Hard and Soft Ions

The hardness, η , of an atom or ion can also provide us with information about the chemistry that will happen between different reagents. In general, hard acids tend to form compounds with hard bases and soft acids tend to bind to soft bases.

Hard acids include transition metals and main group elements that are small and highly charged e.g. Li^+ , Mg^{+2} , Al^{+3} , Fe^{+3}

Hard bases generally contain main group elements that are small and very electronegative e.g. F^- , R-O^- , NH_3 , Cl^-

Soft acids include transition metals and main group elements that are large and not as highly charged e.g. Tl^+ , Ag^+ , Pb^{+2} , Fe^{+2}

Soft bases generally contain main group elements that are large and weakly electronegative e.g. I^- , SR_2 , AsR_3 , $\text{R-N}\equiv\text{C}$

You can find a table of hard and soft acids and bases in Chapter 7 of H&S (table 7.9). You will learn more about the utility of hardness in Chemistry 251.