7.11: Electronegativity

The ability of an atom in a molecule to attract a shared electron pair to itself, forming a polar covalent bond, is called its **electronegativity**. The negative side of a polar covalent bond corresponds to the *more electronegative* element. Furthermore the more polar a bond, the larger the *difference* in electronegativity of the two atoms forming it.

Unfortunately there is no direct way of measuring electronegativity. Dipole-moment measurements tell us about the electrical behavior of *all* electron pairs in the molecule, not just the bonding pair in which we are interested. Also, the polarity of a bond depends on whether the bond is a single, double, or triple bond and on what the other atoms and electron pairs in a molecule are. Therefore the dipole moment cannot tell us quantitatively the difference between the electronegativities of two bonded atoms. Various attempts have been made over the years to derive a scale of electronegativities for the elements, none of which is entirely satisfactory. Nevertheless most of these attempts agree in large measure in telling us which elements are more electronegative than others. The best-known of these scales was devised by the Nobel prize-winning California chemist Linus Pauling (1901 to 1994) and is shown in the periodic table found below. In this scale a value of 4.0 is arbitrarily given to the most electronegative element, fluorine, and the other electronegativities are scaled relative to this value.

Periodic Table

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group (vertical)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
Period (horizontal)																		
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 2.60
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 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo
Lanthanoids	*	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		

Actinoids	**	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

As can be seen from this table, elements with electronegativities of 2.5 or more are all nonmetals in the top right-hand comer of the periodic table. These have been color-coded dark red. By contrast, elements with negativities of 1.3 or less are all metals on the lower left of the table. These elements have been coded in dark gray. They are often referred to as the most **electropositive** elements, and they are the metals which invariably form binary ionic compounds. Between these two extremes we notice that most of the remaining metals (largely transition metals) have electronegativities between 1.4 and 1.9 (light gray), while most of the remaining nonmetals have electronegativities between 2.0 and 2.4 (light red). Another feature worth noting is the very large differences in electronegativities in the top right-hand comer of the table. Fluorine, with an electronegativity of 4, is by far the most electronegative element. At 3.5 oxygen is a distant second, while chlorine and nitrogen are tied for third place at 3.0.

If the electronegativity values of two atoms are very different, the bond between those atoms is largely ionic. In most of the typical ionic compounds discussed in the previous chapter, the difference is greater than 1.5, although it is dangerous to attach too much significance to this figure since electronegativity is only a semiquantitative concept. As the electronegativity difference becomes smaller, the bond becomes more covalent. An important example of an almost completely covalent bond between two different atoms is that between carbon (2.5) and hydrogen (2.1).

The properties of numerous compounds of hydrogen and carbon (hydrocarbons) are described in sections on organic chemistry. These properties indicate that the C—H bond has almost no polar character.

✔ Example 7.11.1 : Bond Polarity

Without consulting the table of electronegativities (use the periodic table), arrange the following bonds in order of decreasing polarity: B—Cl, Ba—Cl, Be—Cl, Br—Cl, Cl—Cl.

Solution

We first need to arrange the elements in order of increasing electronegativity. Since the electronegativity increases in going up a column of the periodic table, we have the following relationships:

Ba < Be and Br < Cl

Also since the electronegativity increases across the periodic table, we have

Be < B

Since B is a group III element on the borderline between metals and non-metals, we easily guess that

B < Br

which gives us the complete order

Ba < Be < B < Br < Cl

Among the bonds listed, therefore, the Ba—Cl bond corresponds to the largest difference in electronegativity, i.e., to the most nearly ionic bond. The order of bond polarity is thus

Ba—Cl > Br—Cl > B—Cl > Br—Cl > Cl—Cl

where the final bond, Cl—Cl,is, of course, purely covalent.