

GENERAL CHEMISTRY

Lesson 7

Electronegativity. Non-polar and polar bonds. Oxidation state. Oxidation and reduction. Oxidation state and valence.

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1 Non-polar and polar bonds. Covalent and ionic bonds

1.1 Non-polar covalent bond

When two atoms hydrogen atoms form a covalent bond, the electron pair they share is distributed evenly among these atoms. In other words, each electron spend equal time around the first and the second hydrogen atom. That means, *electronic density*, or the “density” of electronic clouds around each atom is the same, so the effective electric charge of both atom is also the same. There is no negatively or positively charged poles in the H_2 molecule, so the bond between two hydrogen atoms is *non-polar*. The same is true for O_2 , N_2 , F_2 , S_8 , and other molecules formed by the atoms of the same type.

1.2 Polar covalent bond

When the chemical bond is formed between two different atoms, the situation is different. For example, in the HF molecule, fluorine attracts its electrons stronger than hydrogen, so each electron in the electron pair these two atoms share will spend more time near the fluorine atom than near the hydrogen atom. As a result, hydrogen acquires partial positive charge¹, and the fluorine atom becomes partially negative. This bond is called a *polar covalent bond*.

Polarity of the chemical bond can be predicted based on the property called *electronegativity*, i.e. the ability to attract an additional electron. Although this parameter correlates with the ionization energy (the energy needed to take one electron from an isolated atom, the parameter we discussed before), but these two parameters are not exactly the same. In

¹“Partial positive charge” means this charge is smaller than the charge of a single electron. Although the charge of an electron is a minimal possible charge of an individual particle, we can speak about “partial charge” because it reflects the difference between the electronic density (which is negative) and the effective positive charge of the nucleus. Since the electronic density of a certain part of a molecule can vary continuously (provided that the whole molecule remains neutral), “partial electric charge” can take any values from zero to the charge of a single electron.

contrast to the ionisation energy, electronegativity cannot be measured directly, it is partially derived from some experimental data, and partially calculated. The electronegativity for all elements, expressed in arbitrary units, is shown below.

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
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 1.87	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	Ff	Uup	Lv	Uus	Uuo
			*	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
			**	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

From this table, we can conclude that fluorine is the most electronegative element, and francium is the most electropositive element (i.e. it prefers to donate electrons when it binds to any other atom). It is also easy to see from this table that electronegativity increases when we move from the left side of each period to the right, and when we move from the bottom of each group to the top².

1.3 Ionic bond

When two elements with very different electronegativity form a chemical bond, the electron pair may migrate almost completely to the atom with greater electronegativity. For example, in the francium fluoride (FrF), the electron pair almost is completely shifted to fluorine. As a result, the charge of the fluorine atom becomes almost exactly -1, and the charge of the francium atom becomes +1. Since the atoms having the positive or negative charge (multiple of the charge on a single electron) are called *ions*, we can conclude that formation of the chemical bond between the fluorine and francium atom is accompanied for their *ionization*.

Since the electron pair in FrF belongs almost exclusively to fluorine, we cannot speak about the central electronic cloud that holds two atoms together. In the compounds of that type, the force responsible for chemical bond formation is a simple electrostatic force, i.e. just a Coulomb attraction between the positive francium ion and the negative fluorine ion. This type interaction is called an *ionic bond*.

1.4 Transition between the ionic and the covalent bond

²There are few exceptions from that observations.

Does it mean francium donates its outer electron to fluorine *completely*? Actually, no. Although electronegativities of these two elements are dramatically different, francium's electron does spend some small fraction of time around the francium atom. However, lion's share of time it spend near fluorine, and that is why francium fluoride is considered an ionic compound. The situation with other elements is more complex, because there is no strict and sharp border between the polar covalent and ionic bonds, so each chemical bond is partially ionic and partially covalent. The electronegativity difference of 1.7 approximately corresponds to the parity between the ionic and the covalent nature of the chemical bond. Accordingly, it would be correct to consider the bond between oxygen and carbon a (polar) covalent bond (the electronegativity difference between O and C is ca 0.9), whereas the bond between oxygen and sodium (the electronegativity difference ca 2.5) is predominantly ionic.

2 Oxidation and oxidation states.

Last year, we did the experiments with oxygen, and we found oxygen can form oxides with many substances during the process called *combustion*. We also made a more general conclusion and introduced the term “oxidation”, which we defined as “addition of oxygen to some element or compound”. If we look at the simple example of oxidation, for example, combustion of magnesium in an oxygen atmosphere,



we see that during this process the electrons are being transferred from the magnesium atom to the oxygen atom, so the ionic compound MgO is formed.

In the another example of the oxidation reaction, combustion of carbon,

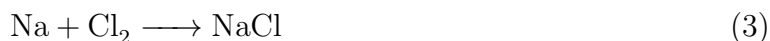


the product is not an ionic compound. However, in that case oxygen also acquire electrons from carbon, although it does not take away completely from the carbon atom. Nevertheless, the electronic density becomes displaced from the carbon atom to the oxygen atom, so the former becomes partially positive, and the latter becomes partially negative.

Analysis of many examples of oxidation demonstrates that in all case the electrons are being transferred (completely or partially) from the atom that is being oxidized (a *reducer*, or *reductant*), to the *oxidizer* atom. During this process, the oxidant is being *reduced* (i.e. it acquires electrons from the reducer). Accordingly, any chemical reaction accompanied by the transfer of electrons from the reducer to the oxidant is called *oxidation reaction*, or, more correctly, a *redox* reaction (“Red-Ox” is a combination of two words: **r**eduction and **o**xidation). Based on this definition we can conclude that not only oxygen, but many other chemical substances can act as oxidizers. For example, fluorine is even more active oxidizer than oxygen: almost any element (except helium, neon and argon) can be oxidized by fluorine, and even oxygen itself can burn in the fluorine atmosphere to form oxygen fluoride (O_2F_2).

2.1 Oxidation state

To qualitatively characterize the outcome of the redox reaction, a term “oxidation state” is used. An oxidation state of an elementary substance in a free form equals to zero. If we consider a reaction between sodium and chlorine (sodium burns in the atmosphere of chlorine like magnesium burns in oxygen), we will see that one electron is being transferred from sodium to chlorine:



Obviously, sodium is being oxidized during this process, and its oxidation state equals to its electric charge (+1) in the product (NaCl). Accordingly, oxidation state of chlorine changes from 0 (in Cl_2) to -1.

For covalent compounds, for example, for CO_2 , calculation of the oxidation state is a little bit more complex. The actual electric charge on each atom is much smaller than 1, so the oxidation state is calculated *assuming* each bond is ionic. For example, in CO_2 , carbon forms four bonds with oxygen atoms, and each of these bonds is polar. Since the electronic density is displaced towards oxygen, we assume each bond corresponds to the oxidation state +1. That means, oxidation state of carbon in CO_2 equals to +4, and the oxidative state of oxygen equals to -2. Of course, that does not mean this compound is ionic. Oxidation state is a formal parameter, however, it is useful for many practical purposes.

And finally, it is easy to demonstrate that the sum of all oxidation states of each atom in a neutral molecule must be equal to zero.

Homework

1. Using the electronegativity table, tell which of the below compounds are ionic and which are covalent:

K_2O , CuCl_2 , ICl , BF_3 , Na_2S , SiO_2 , CaBr_2 , PF_5 .

2. Draw structural formulas of the compounds shown below and predict the sign of the electric charge on each atom of their molecules³

H_2SO_4 , HCl , IF_3 , GaAs , H_3PO_4 , HNO_3 .

3. Calculate oxidation states for each atom in the following compounds⁴:

KMnO_4 , CCl_4 , H_2SeO_4 , PBr_5 .

If you have any questions, feel free to ask.
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³If you do not remember how to write structural formulas, look at the reading materials (HW1).

⁴I recommend you to draw structural formulas for that