1.1: Oxidation State

Electron transfer is one of the most basic processes that can happen in chemistry. It simply involves the movement of an electron from one atom to another. Many important biological processes rely on electron transfer, as do key industrial transformations used to make valuable products. In biology, for example, electron transfer plays a central role in respiration and the harvesting of energy from glucose, as well as the storage of energy during photosynthesis. In society, electron transfer has been used to obtain metals from ores since the dawn of civilization.

Oxidation state is a useful tool for keeping track of electron transfers. It is most commonly used in dealing with metals and especially with transition metals. Unlike metals from the first two columns of the periodic table, such as sodium or magnesium, transition metals can often transfer different numbers of electrons, leading to different metal ions. Sodium is generally found as Na^+ and magnesium is almost always Mg^{2+}, but manganese could be Mn^{2+}, Mn^{3+}, and so on, as far as Mn^{7+}.

At first glance, "oxidation state" is often synonymous with "charge on the metal". However, there is a subtle difference between the two terms. For example, in a coordination complex, a metal atom that is ostensibly an ion with a charge of +2 may have very little charge on it at all. Instead, the positive charge may be delocalized onto the ligands that are donating their own electrons to the metal. Oxidation state is used instead to describe what the charge on the metal ion would be if the coordinated ligands were removed and the metal ion left by itself.

Oxidation state is commonly denoted by Roman numerals after the symbol for the metal atom. This designation can be shown either as a superscript, as in Mn^{II}, or in parentheses, as in Mn(II); both of these descriptions refer to a Mn^{2+} ion, or what might have been a Mn^{2+} ion before it got into a bonding situation.

Exercise 1.1.1

Translate the following oxidation state descriptions into charges on the metal.

a) Ag^{I} b) Ni(II) c) Mn^{VII} d) Cr(VI) e) Cu(III) f) Fe^{IV} g) Os^{VIII} h) Re(V)

Answer a

a) Ag^+

Answer b

b) Ni^{2+}

Answer c

c) Mn^{7+}

Answer d

d) Cr^{6+}

Answer e

e) Cu^{3+}

Answer f

f) Fe^{4+}

Answer g

g) Os^{8+}

Answer h

h) Re^{5+}

Exercise 1.1.2

a. Provide the valence shell electron configuration for each metal species in the previous question (e.g. oxygen's is $2s^2 2p_x^2 2p_y^1 2p_z^1$).

b. Draw an energy level diagram showing the occupation of valence s, p and d levels for each metal species in the previous question.

The oxidation state of a metal within a compound can be determined only after the other components of the compound have been conceptually removed. For example, metals are frequently found in nature as oxides. An oxide anion is O^{2-}, so every oxygen in a compound will correspond to an additional 2- charge. In order to balance charge, the metal must have a corresponding plus charge.

For example, sodium oxide has the formula Na_2O. If the oxygen ion is considered to have a 2- charge, and there is no charge overall, there must be a corresponding charge of +2. That means each sodium ion has a charge of +1.

? Exercise 1.1.3

Determine the charge on the metal in each of the following commercially valuable ores. Note that sulfur, in the same column of the periodic table as oxygen, also has a 2- charge as an anion.

a) galena, PbS b) cassiterite, SnO_2 c) cinnabar, HgS d) pyrite, FeS_2 e) haematite, Fe_2O_3 f) magnetite, Fe_3O_4

Answer a

a) Pb^{2+} & S^{2-}

Answer b

b) Sn^{4+} & 2 O^{2-}

Answer c

c) Hg^{2+} & S^{2-}

Answer d

d) Fe^{4+} & 2 S^{2-}

Answer e

e) 2 Fe^{3+} & 3 O^{2-}

Answer f

f) 2 Fe^{3+} & 1 Fe^{2+} & 4 O^{2-}

? Exercise 1.1.4

Sphalerite is a common zinc ore, ZnS. However, sphalerite always has small, variable fractions of iron in place of some of the zinc in its structure. What is the likely oxidation state of the iron?

Answer

Probably Fe^{2+}, to replace Zn^{2+} ions.

? Exercise 1.1.5

Sometimes non-metals such as carbon are thought of in different oxidations states, too. For example, the coke used in smelting metal ores is roughly C, in oxidation state 0. Determine the oxidation state of carbon in each case, assuming oxygen is always 2- and hydrogen is always 1+.

a) carbon monoxide, CO b) carbon dioxide, CO_2 c) methane, CH_4 d) formaldehyde, H_2CO e) oxalate, $C_2O_4^{2-}$

Answer a

a) C^{2+}

Answer b

b) C^{4+}

Answer c

c) C^{4-}

Answer d

d) C^{0}

Answer e

e) C^{3+}

? Exercise 1.1.6

Sometimes it is useful to know the charges and structures of some of the earth's most common anions. Draw Lewis structures for the following anions:

a) hydroxide, HO^{-} b) carbonate, CO_3^{2-} c) sulfate, SO_4^{2-} d) nitrate, NO_3^{-}

e) phosphate, PO_4^{3-} f) silicate, SiO_4^{4-} g) inosilicate, SiO_3^{2-}

? Exercise 1.1.7

Use your knowledge of common anions to determine the oxidation states on the metals in the following ores.

a) dolomite, $MgCO_3$ b) malachite, $Cu_2CO_3(OH)_2$ c) manganite, $MnO(OH)$

d) gypsum, $CaSO_4$ e) rhodochrosite, $MnCO_3$ f) rhodonite, $MnSiO_3$

Answer a

a) Mg^{2+}

Answer b

b) Cu^{2+}

Answer c

c) Mn^{3+}

Answer d

d) Ca^{2+}

Answer e

e) Mn^{2+}

Answer f

f) Mn^{2+}

? Exercise 1.1.8

In mixed-metal species, the presence of two different metals may make it difficult to assign oxidation states to each. For the following ores, propose one solution for the oxidation states of the metals.

a) chalcopyrite, $CuFeS_2$ b) franklinite, $ZnFe_2O_4$ c) beryl, $Be_3Al_2(SiO_3)_6$ d) bornite or peacock ore, Cu_5FeS_4

e) turquoise, $CuAl_6(PO_4)_4(OH)_8$

Answer a

a) Cu(II), Fe(II)

Answer b

b) Zn(II), Fe(III)

Answer c

c) Be(II), Al(III)

Answer d

d) Cu(I), Fe(III)

Answer e

e) Cu(II), Al(III)

? Exercise 1.1.9

Feldspars are believed to make up about 60% of the earth's crust. The alkali, alkaline earth and aluminum metals in these tectosilicates are typically found in their highest possible oxidation states. What are the charges on the silicates in the following examples?

a) orthoclase, $KAlSi_3O_8$ b) anorthite, $CaAl_2Si_2O_8$ c) celsian, $BaAl_2Si_2O_8$ d) albite, $NaAlSi_3O_8$

? Exercise 1.1.10

Frequently, minerals are solid solutions in which repeating units of different compositions are mixed together homogeneously. For example, labradorite is a variation of anorthite in which about 50% of the aluminum ions are replaced by silicon ions and about 50% of the calcium ions are replaced by sodium ions. Show that this composition would still be charge neutral overall.