3.3: Oxidation and Reduction

Oxidation number

The **oxidation number** is the formal electrical charge of a component atom in a compound or in an ion allocated in such a way that the atom with smaller electronegativity has a positive charge. Since electrical charges do not differ in the case of a molecule composed of the same atoms, the oxidation number of the atoms is the quotient of the net electrical charge divided by the number of atoms. In the case of a compound or an ion consisting of different atoms, the atoms with larger electronegativity can be considered as anions and those with smaller electronegativity as cations. For example, nitrogen is 0 valent in N_2; oxygen is -1 in O_2^{2-}; nitrogen is +4 and oxygen -2 in NO_2; but nitrogen is -3 and hydrogen +1 in NH_3. That is, the oxidation number can be different for the same atom combined with different partners and the atom is said to be in the formal oxidation state corresponding to that oxidation number. Although this does not express the quantitative deviation of the actual electric charge, it is convenient in counting valence electrons or in dealing with redox reactions.

Exercise 3.3.1

Which halogen has the largest oxidizing power?

Answer

Since the reduction potential of fluorine is the highest, its oxidizing power is the largest.

Redox reactions

Originally, oxidation meant the formation of oxides from elements or the formation of compounds by the action of oxygen, and reduction is the reverse of oxidation. The present definition of **reduction** is a reaction which gives an electron, and **oxidation** is the reaction which takes an electron. Therefore, a reagent which gives an electron is a **reductant** and one which takes an electron is an **oxidant**. As a result of a redox reaction, a reductant is oxidized and an oxidant is reduced. For example, in the reaction of molybdenum metal and chlorine gas to form molybdenum pentachloride, molybdenum is a reductant and changes its oxidation state from 0 to +5 and chlorine is an oxidant and changes its oxidation state from 0 to -1.

$$2\ Mo + 5\ Cl_2 \rightarrow Mo_2Cl_{10}$$

Latimer diagram

A **Latimer diagram** is a diagram in which the chemical species in the highest oxidation state is placed at the left end and a series of the reduced chemical species of the same atom are arranged to the right-hand side in the order of the oxidation states, and the standard reduction potentials (/V) are written above the line which connects each state. This diagram is convenient for discussing a redox reaction. Since electric potential differs between an acidic and a basic solution, different diagrams are required depending on the pH of the solution. Taking the series of the oxides and hydrides of nitrogen in acidic solution as an example,

$$\overset{+5}{NO_3^-} \xrightarrow{0.803} \overset{+4}{N_2O_4} \xrightarrow{1.07} \overset{+3}{HNO_2} \xrightarrow{0.996} \overset{+2}{NO} \xrightarrow{1.59} \overset{+1}{N_2O} \xrightarrow{1.77} \overset{0}{N_2}$$
$$\xrightarrow{-1.87} \overset{-1}{NH_3OH^+} \xrightarrow{1.41} \overset{-2}{N_2H_5^+} \xrightarrow{1.275} \overset{-3}{NH_4^+}$$

in a basic solution, the series becomes

$$\overset{+5}{NO_3^-} \xrightarrow{-0.86} \overset{+4}{N_2O_4} \xrightarrow{0.867} \overset{+3}{NO_2^-} \xrightarrow{-0.46} \overset{+2}{NO} \xrightarrow{0.76} \overset{+1}{N_2O} \xrightarrow{0.94} \overset{0}{N_2}$$
$$\xrightarrow{-3.04} \overset{-1}{NH_2OH} \xrightarrow{0.73} \overset{-2}{N_2H_4} \xrightarrow{0.1} \overset{-3}{NH_3}$$

The additivity of the state function ΔG^0 is used in order to calculate the standard reduction potential between remote oxidation states.

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

$$-(n_1 + n_2)FE^0 = -n_1FE_1^0 - n_2FE_2^0$$

Where the free energy change and electric potential between adjacent states are $\Delta G_1^0, E_1^0, \Delta G_2^0, E_2^0$, respectively, and the number of transferred electrons n_1, n_2. Namely,

$$E^0 = \frac{n_1 E_1^0 + n_2 E_2^0}{n_1 + n_2}$$

For example, in the reduction of NO_3^- to HNO_2, two electrons are transferred to form HNO_2 via N_2O_4 and the potential becomes

$$E^0 = \frac{0.803\ V + 1.07\ V}{2} = 0.94\ V$$

? Exercise 3.3.2

Calculate the reduction potential of the reduction of NO_3^- to NO_2^- in a basic solution.

Answer

$$E^0 = \frac{-0.86\ V + 0.867\ V}{2} = 0.004\ V$$

In recent years, whenever a new inorganic compound is synthesized, its redox properties are investigated, usually by electrochemical measurements. **Cyclic voltammetry** is the technique of choice for the study of its redox properties, including the electric potential, the number of transferred electrons, and the reversibility of the reactions, etc. because of the simplicity of the measurements. It is approximately correct to consider that the oxidation potential corresponds to the energy level of the HOMO, because oxidation usually takes an electron from the HOMO and the reduction potential to the level of the LUMO since reduction adds an electron to the LUMO. However, various factors, such as solvent effects, should be taken into consideration during quantitative discussions of redox processes.