3.1: Thermodynamics

Thermodynamic parameters on changes of state are necessary to describe chemical bonding, structure, and reaction. This is true also in inorganic chemistry, and the most important concepts in thermodynamics are described in this section. Even simple thermodynamic knowledge is considerably useful for judging whether structures of compounds are stable and the likelihood of spontaneous reactions, and for the calculations of reaction heat, determination of reaction mechanism, and understanding of electrochemistry.

Enthalpy

Since enthalpy is the heat content of a system under constant pressure, the changeΔH is negative in an exothermic reaction, and positive in an endothermic reaction. The standard reaction enthalpy, ΔH^0, is the enthalpy change between 1 mol of products and reactants in the standard state (10^5 Pa and 298.15 K). The **standard enthalpy of formation**, ΔH_f^0, of a compound is the standard reaction enthalpy for the formation of the compound from its constituent elements. Since enthalpy is a state function, the standard reaction enthalpy is calculated by defining the standard enthalpy of formation of simple substances to be zero. Namely,

$$\Delta H^0 = \Sigma n \Delta H_f^0 \ (product) - \Sigma n \Delta H_f^0 \ (reactant)$$

Entropy

Entropy is a state function, and is a criterion determining whether one state can be reached spontaneously from another state. The 2nd law of thermodynamics states that the entropy, S, of an isolated system increases upon a spontaneous change. Namely,

$$\Delta S > 0$$

A thermodynamically irreversible process produces entropy. Entropy is related to the disorder of a system in statistical themodynamics as follows:

$$S = k \ln W$$

k is the Boltzmann constant, and W is the number of the arrangements of atoms or molecules of the system with the same energy, and corresponds to the extent of disorder. As entropy becomes larger, the larger the disorder of a system.

Gibbs energy

This quantity is defined as

$$\Delta G = \Delta H - T \Delta S$$

A spontaneous reaction occurs when Gibbs energy of a reaction is negative at constant temperature and pressure. The standard Gibbs free energy ΔG^0 is related to the equilibrium constant K of the reaction

$$A \overset{K}{\rightleftharpoons} B.$$

$$\Delta G^0 = -RT \ln K$$

K is larger than 1 when ΔG^0 becomes negative, and the reaction proceeds to the right.