3.2: Electrochemistry

The **standard state** is defined as the one corresponding to 25° C (298.15 K), unit activity for all the substances in an electrochemical zero-current cell under 1 bar of pressure (10^5 Pa). For a reaction in which H+ ions participate, the standard state is pH = 0 (approximately 1 mol acid).

In the hydrogen electrode used as the standard of electrode potential, 1 atm of hydrogen gas (a_{H^+} = 1) is slowly contacted with a platinum-black electrode immersed in a strong acid solution of activity a_{H2} = 1. The potential is expressed as

$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{a_{H_2}}$$

and by definition E^0 = 0 in the standard state. The hydrogen electrode in the standard state is called the **standard hydrogen electrode**, or NHE. Although reduction potential is usually expressed with reference to the NHE standard, the hydrogen electrode is inconvenient to handle. Therefore a **saturated calomel (SCE)** or an Ag / AgCl electrode is used as a reference electrode for everyday electrochemical measurements and experimental potentials are measured against these electrodes or converted into NHE values. When the NHE value is set to 0, the SCE value is 0.242 V, and the Ag/AgCl value is 0.199 V.

A redox reaction takes place only when redox partners exist and a reactant can be either an oxidant or reductant depending on its reaction partner. The relative redox capability can be expressed numerically by introducing the reduction potentials E^0 of imaginary half-reactions (Table 3.2.1). The free energy change ΔG^0 of a reaction is related to E^0,
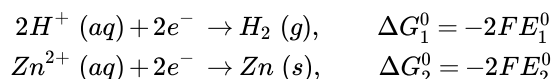
$$\Delta G^0 = -nFE^0$$

where n is the number of transferred electrons and F the Faraday constant 96500 C mol^{-1}.

Table 3.2.1: Standard reduction potentials at 25 °C

Couple	E° / V
$F_2(g) + 2e^- \rightarrow 2F^- (aq)$	+2.87
$H_2O_2(aq) + 2H^+ (aq) + 2e^- \rightarrow 2H_2O(l)$	+1.77
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	+1.72
$MnO_2^- (aq) + 8H^+ (aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Cl_2(g) + 2e^- \rightarrow 2Cl^- (aq)$	+1.36
$O_2(g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightarrow 2Br^- (aq)$	+1.09
$Fe^{3+}(aq) + e- \rightarrow Fe^{2+}(aq)$	+0.77
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^- (aq)$	+0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+ (aq)$	+0.15
$2H^+ (aq) + 2e^- \rightarrow H_2(g)$	0
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Na^+ (aq) + e^- \rightarrow Na(s)$	-2.71
$Li^+ (aq) + e^- \rightarrow Li(s)$	-3.04

For example, the two reactions

$$2H^+ \ (aq) + 2e^- \ \to H_2 \ (g), \qquad \Delta G_1^0 = -2FE_1^0$$
$$Zn^{2+} \ (aq) + 2e^- \ \to Zn \ (s), \qquad \Delta G_2^0 = -2FE_2^0$$

do not occur independently, but if both H$^+$ (aq) and Zn (s) are present, the redox reaction takes place. The equation for the actual reaction is complete when the latter equation is subtracted from the former.

$$2H^+ \ (aq) + Zn \ (s) \to H_2 \ (g) + Zn^{2+} \ (aq)$$
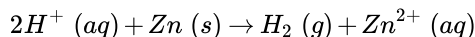
The free energy change of the whole redox reaction is the difference between $\Delta G_1^0, \Delta G_2^0$ for the respective half-reactions.

$$\Delta G^0 = \Delta G_1^0 - \Delta G_2^0$$
$$= -2F(E_1^0 - E_2^0)$$

Because half-reactions are not real and they are used in pairs, the free energy change of ΔG_1^0 H$^+$ is set to zero for convenience. Since the experimental value of ΔG^0 is -147 kJ, equals 147 kJ. Potential ΔG_2^0 corresponding to ΔG^0 of a half-reaction is called the **standard reduction potential**.

$$E^0 = -\frac{\Delta G^0}{nF}$$

Therefore,

$$E^0(H^+, H_2) = 0 \quad \text{(by definition)}$$
$$E^0(Zn^{2+}, Zn) = \frac{-147 \ kJ/mol}{2 \times 96500 \ C/mol} = -0.76 \ V$$
$$(1 \ J = 1 \ C \cdot V).$$

The standard potentials of various half-reactions are determined using similar procedures to that mentioned above (Table 3.2.1). The E^0 s of redox reactions can be calculated by combining E^0 of these half-reactions.

If E^0 of a redox reaction is positive, ΔG^0 is negative and the reaction occurs spontaneously. Consequently, instead of the free energy change the difference in reduction potentials can be used to judge the thermodynamic spontaneity of a reaction. The higher the reduction potential of a reagent the stronger its oxidation ability. The positive or negative signs are based on the expedient of setting the reduction potential of a proton to 0, and it should be understood that a positive sign does not necessarily mean oxidizing, and a negative sign reducing. The series arranged in the order of redox power is called the **electrochemical series**.