Zedelius *et al*.

Appendix S2

Redox potentials of subsequent reduction steps, and average redox potential

If an electron acceptor A_{ox} is reduced stepwise to A_{red} via m subsequent steps involving free intermediates (I_i), the reaction can be written as follows (n_i, number of electrons):

$$A_{ox} \xrightarrow{n_1\, e^-} I_1 \xrightarrow{n_2\, e^-} I_2 \quad \cdots \quad I_{m-1} \xrightarrow{n_m\, e^-} A_{red}$$

With an electron donor of a given redox potential, E_{don}, and the redox potential E_i of a reduction step (definition of which is originally based on a reversible reaction), the free energy change of an individual step is $-\Delta G_i = n_i\, F\, \Delta E_i = n_i\, F\, (E_i - E_{don})$; $F = 96{,}485$ C mol^{-1} (Faraday constant). The free energy change of the total reduction reaction is

$$-\Delta G_{tot} = n_1\, F\, (E_1 - E_{don}) + n_2\, F\, (E_2 - E_{don}) + \ldots + n_m\, F\, (E_m - E_{don}) \tag{1}$$

$$= F\, [(n_1E_1 + n_2E_2 + \ldots + n_mE_m) - (n_1 + n_2 + \ldots + n_m)E_{don}] \tag{2}$$

The sum $n_1 + n_2 + \ldots + n_i$ is the total number of electrons, n_{tot}, so that

$$-\Delta G_{tot} = F\, [(n_1E_1 + n_2E_2 + \ldots + n_mE_m) - n_{tot}E_{don}]\ . \tag{3}$$

Rearrangement leads to

$$\frac{-\Delta G_{tot}}{n_{tot}\, F} + E_{don} = \frac{n_1E_1 + n_2E_2 + \ldots + n_mE_m}{n_{tot}}\ . \tag{4}$$

The term $-\Delta G_{tot}/(n_{tot}\, F)$ expresses a redox potential difference. Because it includes only parameters referring to the total reaction, it can be defined as the average redox potential difference, ΔE_{av}, of the total reaction:

$$\frac{-\Delta G_{tot}}{n_{tot}\, F} = \Delta E_{av}\ . \tag{5}$$

Because ΔE_{av} is relative to the redox potential of the donor reaction, (5) necessarily defines also an average redox potential by $\Delta E_{av} = E_{av} - E_{don}$. We can thus write (4) as

$$(E_{av} - E_{don}) + E_{don} = E_{av} = \frac{n_1E_1 + n_2E_2 + \ldots + n_mE_m}{n_{tot}} \tag{6}$$