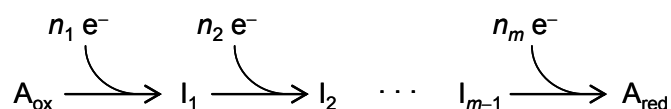


## Appendix S2

## 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):



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  $-\Delta G_i = n_i F \Delta E_i = n_i F (E_i - E_{don})$ ;  $F = 96,485 \text{ C mol}^{-1}$  (Faraday constant). The free energy change of the total reduction reaction is

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

$$= F [(n_1 E_1 + n_2 E_2 + \dots + n_m E_m) - (n_1 + n_2 + \dots + n_m) E_{don}] \quad (2)$$

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

$$-\Delta G_{tot} = F [(n_1 E_1 + n_2 E_2 + \dots + n_m E_m) - n_{tot} E_{don}] . \quad (3)$$

Rearrangement leads to

$$\frac{-\Delta G_{tot}}{n_{tot} F} + E_{don} = \frac{n_1 E_1 + n_2 E_2 + \dots + n_m E_m}{n_{tot}} . \quad (4)$$

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,  $\Delta E_{av}$ , of the total reaction:

$$\frac{-\Delta G_{tot}}{n_{tot} F} = \Delta E_{av} . \quad (5)$$

Because  $\Delta E_{av}$  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

$$(E_{av} - E_{don}) + E_{don} = E_{av} = \frac{n_1 E_1 + n_2 E_2 + \dots + n_m E_m}{n_{tot}} \quad (6)$$