Stoichiometry of Biochemical Reactions II

Today's class

- How to write half reactions
- Half reactions - exercises!
- Selecting chemical species of reactants & products in half reactions

Half reactions

- For complex biochemical redox reactions, it is easier to use half reaction approach
- The oxidation reaction for an electron donor and the reduction reaction for an electron acceptor can be splitted
- Usually written as a reduction reaction

Inorganic half-reactions and their Gibb's free energy at pH = 7.0

Textbook Table 2.1

Reaction Number	Reduced-oxidized Compounds	Half-reaction			$\Delta G^{0\prime}$ (kJ/e$^-$ eq)
I-1	Ammonium-nitrate	$\frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	=	$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	-35.11
I-2	Ammonium-nitrite	$\frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	=	$\frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	-32.93
I-3	Ammonium-Nitrogen	$\frac{1}{6}N_2 + \frac{4}{3}H^+ + e^-$	=	$\frac{1}{3}NH_4^+$	26.70
I-4	Ferrous-Ferric	$Fe^{3+} + e^-$	=	Fe^{2+}	-74.27
I-5	Hydrogen-H^+	$H^+ + e^-$	=	$\frac{1}{2}H_2$	39.87
I-6	Nitrite-Nitrate	$\frac{1}{2}NO_3^- + H^+ + e^-$	=	$\frac{1}{2}NO_2^- + \frac{1}{2}H_2O$	-41.65
I-7	Nitrogen-Nitrate	$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	=	$\frac{1}{10}N_2 + \frac{3}{5}H_2O$	-72.20
I-8	Nitrogen-Nitrite	$\frac{1}{3}NO_2^- + \frac{4}{3}H^+ + e^-$	=	$\frac{1}{6}N_2 + \frac{2}{3}H_2O$	-92.56
I-9	Sulfide-Sulfate	$\frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^-$	=	$\frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	20.85
I-10	Sulfide-Sulfite	$\frac{1}{6}SO_3^{2-} + \frac{5}{4}H^+ + e^-$	=	$\frac{1}{12}H_2S + \frac{1}{12}HS^- + \frac{1}{2}H_2O$	11.03
I-11	Sulfite-Sulfate	$\frac{1}{2}SO_4^{2-} + H^+ + e^-$	=	$\frac{1}{2}SO_3^{2-} + \frac{1}{2}H_2O$	50.30
I-12	Sulfur-Sulfate	$\frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^-$	=	$\frac{1}{6}S + \frac{3}{2}H_2O$	19.15
I-13	Thiosulfate-Sulfate	$\frac{1}{4}SO_4^{2-} + \frac{5}{4}H^+ + e^-$	=	$\frac{1}{8}S_2O_3^{2-} + \frac{5}{8}H_2O$	23.58
I-14	Water-Oxygen	$\frac{1}{4}O_2 + H^+ + e^-$	=	$\frac{1}{2}H_2O$	-78.72

Organic half-reactions and their Gibb's free energy at pH = 7.0 (1)

Textbook Table 2.2

Reaction Number	Reduced Compounds	Half-reaction	$\Delta G^{0'}$ (kJ/e$^-$ eq)
O-1	Acetate	$\frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^- = \frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O$	27.40
O-2	Alanine	$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + \frac{1}{12}NH_4^+ + \frac{11}{12}H^+ + e^- = \frac{1}{12}CH_3CHNH_2COO^- + \frac{5}{12}H_2O$	31.37
O-3	Benzoate	$\frac{1}{5}CO_2 + \frac{1}{30}HCO_3^- + H^+ + e^- = \frac{1}{30}C_6H_5COO^- + \frac{13}{30}H_2O$	27.34
O-4	Citrate	$\frac{1}{6}CO_2 + \frac{1}{6}HCO_3^- + H^+ + e^- = \frac{1}{18}(COO^-)CH_2COH(COO^-)CH_2COO^- + \frac{4}{9}H_2O$	33.08
O-5	Ethanol	$\frac{1}{6}CO_2 + H^+ + e^- = \frac{1}{12}CH_3CH_2OH + \frac{1}{4}H_2O$	31.18
O-6	Formate	$\frac{1}{2}HCO_3^- + H^+ + e^- = \frac{1}{2}HCOO^- + \frac{1}{2}H_2O$	39.19
O-7	Glucose	$\frac{1}{4}CO_2 + H^+ + e^- = \frac{1}{24}C_6H_{12}O_6 + \frac{1}{4}H_2O$	41.35
O-8	Glutamate	$\frac{1}{6}CO_2 + \frac{1}{9}HCO_3^- + \frac{1}{18}NH_4^+ + H^+ + e^- = \frac{1}{18}COOHCH_2CH_2CHNH_2COO^- + \frac{4}{9}H_2O$	30.93
O-9	Glycerol	$\frac{3}{14}CO_2 + H^+ + e^- = \frac{1}{14}CH_2OHCHOHCH_2OH + \frac{3}{14}H_2O$	38.88
O-10	Glycine	$\frac{1}{6}CO_2 + \frac{1}{6}HCO_3^- + \frac{1}{6}NH_4^+ + H^+ + e^- = \frac{1}{6}CH_2NH_2COOH + \frac{1}{2}H_2O$	39.80

Organic half-reactions and their Gibb's free energy at pH = 7.0 (2)

Textbook Table 2.2

Reaction Number	Reduced Compounds	Half-reaction	$\Delta G^{0'}$ (kJ/e$^-$ eq)
O-11	Lactate	$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + H^+ + e^- = \frac{1}{12}CH_3CHOHCOO^- + \frac{1}{3}H_2O$	32.29
O-12	Methane	$\frac{1}{8}CO_2 + H^+ + e^- = \frac{1}{8}CH_4 + \frac{1}{4}H_2O$	23.53
O-13	Methanol	$\frac{1}{6}CO_2 + H^+ + e^- = \frac{1}{6}CH_3OH + \frac{1}{6}H_2O$	36.84
O-14	Palmitate	$\frac{15}{19}CO_2 + \frac{1}{92}HCO_3^- + H^+ + e^- = \frac{1}{92}CH_3(CH_2)_{14}COO^- + \frac{31}{92}H_2O$	27.26
O-15	Propionate	$\frac{1}{7}CO_2 + \frac{1}{14}HCO_3^- + H^+ + e^- = \frac{1}{14}CH_3CH_2COO^- + \frac{5}{14}H_2O$	27.63
O-16	Pyruvate	$\frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e^- = \frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O$	35.09
O-17	Succinate	$\frac{1}{7}CO_2 + \frac{1}{7}HCO_3^- + H^+ + e^- = \frac{1}{14}(CH_2)_2(COO^-)_2 + \frac{3}{7}H_2O$	29.09
O-18	Domestic Wastewater	$\frac{9}{50}CO_2 + \frac{1}{50}HCO_3^- + \frac{1}{50}NH_4^+ + H^+ + e^- = \frac{1}{50}C_{10}H_{19}O_3N + \frac{9}{25}H_2O$	*
O-19	Custom Organic	$\frac{(n-c)}{d}CO_2 + \frac{c}{d}HCO_3^- + \frac{c}{d}NH_4^+ + H^+ + e^- = \frac{1}{d}C_nH_aO_bN_c + \frac{2n-b+c}{d}H_2O$ where, $d = 4n + a - 2b - 3c$	*
O-20	Cell Synthesis	$\frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^- = \frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$	*

* Equations O-18 to O-20 do not have $\Delta G^{0'}$ values because the reduced species is not chemically defined.

Writing half reactions

Step 1 Write oxidized form on the left and reduced form on the right

Step 2 Add other species involved in the reaction

Step 3 Balance the reaction for all elements except for oxygen and hydrogen

Step 4 Balance oxygen using water

Step 5 Balance hydrogen using H^+

Step 6 Balance charge using e^-

Step 7 Convert the equation to the e^--equivalent form

Exercise 1: Glucose oxidation

Step 1) →

Step 2) →

Step 3) →

Step 4) →

Step 5) →

Step 6) →

Step 7) →

Exercise 2: Nitrate reduction

Step 1) →

Step 2) →

Step 3) →

Step 4) →

Step 5) →

Step 6) →

Step 7) →

Half reaction for alanine (CH_3CHNH_2COOH)

→

$$\frac{1}{4}CO_2 + \frac{1}{12}NH_3 + H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COOH + \frac{1}{3}H_2O$$

Now, check O-2:

$$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + \frac{1}{12}NH_4^+ + \frac{11}{12}H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COO^- + \frac{5}{12}H_2O \quad \textbf{??}$$

Half reactions – various expressions

Half reaction for alanine can be written as

$$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + \frac{1}{12}NH_4^+ + \frac{11}{12}H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COO^- + \frac{5}{12}H_2O$$

$$\frac{1}{4}CO_2 + \frac{1}{12}NH_3 + H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COOH + \frac{1}{3}H_2O$$

$$\frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + \frac{1}{12}NH_4^+ + H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COOH + \frac{5}{12}H_2O$$

$$\frac{1}{4}HCO_3^- + \frac{1}{12}NH_4^+ + \frac{13}{12}H^+ + e^- \rightarrow \frac{1}{12}CH_3CHNH_2COO^- + \frac{7}{12}H_2O$$

$$\vdots$$

Half reactions – various expressions

Factors of potential consideration:

- Most relevant forms of reactants and products

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ $pK_{a1} = 6.3$

$NH_4^+ \leftrightarrow NH_3 + H^+$ $pK_a = 9.3$

$CH_3CHNH_2COOH \leftrightarrow CH_3CHNH_2COO^- + H^+$ $pK_a = 2.3$

- Simplest form

- Species of interest